VOLUME 9 AUGUST, 1933 NUMBER 2

NATIONAL
RESEARCH COUNCIL
of CANADA

CANADIAN JOURNAL OF RESEARCH

CANADA

Published under the authority
of the
Chairman of the Committee of the
Privy Council on Scientific and Industrial Research

OTTAWA - CANADA

CONTENTS

	PAGE
The Fungi Found in Butter—*G. R. Bisby, M. C. Jamieson and M. Timonin*	97
A Parasitological Survey of the Genus *Citellus* in Manitoba—*J. A. McLeod*	108
Studies on Bacillus Calmette-Guérin (B.C.G.) and Vaccination against Tuberculosis—*E. A. Watson*	128
The Reverification of a Four-metre Rule—*R. H. Field*	137
On the Thermal Conductivity of Various Insulators at Room Temperature—*C. D. Niven*	146
The Sorption of Water by Asbestos Fibre—*L. M. Pidgeon and A. Van Winsen*	153
The Action of Sulphuric Acid on Certain Derivatives of Cyclopropane —*Charles F. H. Allen and Raymond Boyer*	159
Dihydro-*p*-tolualdehyde—*C. F. H. Allen, W. L. Ball and D. M. Young*	169
Pyrolysis of the Lower Paraffins. II. The Production of Olefines in Baffled Quartz Tubes—*Adrien Cambron and Colin H. Bayley*	175

Publications and Subscriptions

The Canadian Journal of Research is published monthly by the National Research Council of Canada, Ottawa, to which address all correspondence should be directed.

The subscription rate is $3.00 per year to any part of the world. Single copies are thirty-five cents each.

Canadian Journal *of* Research

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

VOLUME 9 AUGUST, 1933 NUMBER 2

THE FUNGI FOUND IN BUTTER[1]

BY G. R. BISBY[2], M. C. JAMIESON[3] AND M. TIMONIN[4]

Abstract

Samples of butter from all the creameries in Manitoba were investigated as to mold content. The various species of molds isolated and their relative abundance are listed. A list of fungi recorded as occurring in butter is given. It is pointed out that fungi of various kinds may enter butter, and some of them may develop objectionable colonies when butter is held for some time in transportation or storage. Certain creameries are reported as producing butter practically free from fungi, and suggestions are given regarding methods of lessening the development of molds in butter.

Introduction

During recent years buttermakers in Manitoba and other parts of Canada have endeavored to produce butter of increasingly high quality. The results achieved have been excellent for the most part, but one rather serious source of trouble arose when butter was shipped to England: molds developed in a number of these shipments. The importance of preventing moldiness in Canadian butter is emphasized by Hood and White (8).

Dairy bacteriologists in Manitoba have determined, for several successive years, the prevalence of molds in representative samples of butter from various creameries, and have aided the buttermakers in their efforts to reduce the numbers of fungi to a minimum. This article presents an analysis of the identity and prevalence of molds found in butter during 1932, and suggests preventive measures. The work was done in conjunction with work on soil fungi (1), since the majority of the fungi found in butter occur also in soil. Many of the species isolated have not been recorded previously in dairy products.

The literature dealing with molds in butter, up to 1929, is summarized by Macy (9), who made extensive experiments to determine the food supply of certain fungi found in butter, and the relation of moisture, temperature, air supply, and salt to mold development. Macy presents a list of the fungi recorded from butter. Grimes, Kennelly and Cummins identified many fungi found in butter (6) and milk (4) in Ireland, and studied their growth on various media. A later paper from Ireland (7) deals with species of *Phoma* found in

[1] *Manuscript received May 18, 1933.*
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butter. Molds in butter are also being investigated in New Zealand (12) and elsewhere.

The results reported in this paper were obtained from two types of creamery butter made from pasteurized cream. One was the regular creamery output, the other a special product made painstakingly by certain creameries for competition purposes.

The samples of butter from which isolations were made, were taken at the time of grading by staff members of the Provincial and Federal Dairy Branches. Four, three, or two samples per month, depending on the quantity manufactured, were taken from each of the 55 creameries of Manitoba. Due care was taken to avoid external contamination when sampling. A wrapped sterile knife was used to cut each sample of about two ounces, taken from diagonally opposite corners of the parchment-lined boxes of butter. By this method three exterior surfaces were included in each case. The samples were placed at once in sterile screw-top jars, and kept in a refrigerator until analyzed.

Mold and yeast counts were made by the technique of the Committee on Bacteriological Analysis of Dairy Products (3). In this paper, yeast counts are not included under the heading of "molds". The samples were carefully melted to a creamy consistency, and platings made from 1 cc. and 1/10 cc. of butter, using Difco malt agar medium acidified to a pH of 3.5 (14). Incubation was at 25° C. for five days (15). Counts were then made and recorded on a cubic centimetre basis.

Colonies of fungi to be identified were taken from certain plates to test tubes. As far as possible, one plate per month from each creamery was selected for these transfers, and in addition any colonies that appeared to be different were removed from extra plates. Non-acidified Czapek's agar slopes were used except for Mucorales, which were transferred to tubes of Waksman's agar, and *Oospora* and *Mycoderma* which were placed on malt agar slopes. These cultures were incubated at 25° C. until growth was sufficient to permit of a taxonomic study.

The Number of Molds Found in Butter

During the summer of 1932, 858 samples of butter were studied. Table I lists the samples arranged according to numbers of molds found.

TABLE I

NUMBERS OF MOLDS FOUND IN SAMPLES OF BUTTER

Number of molds per cc.	Number of samples	Per cent of total
None found	258	30.1
1 to 10	388	45.2
11 to 100	164	19.1
Over 100	48	5.6
Total	858	100.0

Table I shows that nearly one-third of the samples of butter had been made with such care that no contaminating molds developed on the plates. Three-fourths of the samples contained not more than ten molds per cc. of butter.

Table II gives the results obtained in 1932 by a few creameries representative of various degrees of efficiency in controlling mold contamination.

TABLE II

CLASSIFICATION OF CERTAIN CREAMERIES ACCORDING TO NUMBERS OF MOLDS FOUND

Creamery	Samples classified according to numbers of molds per cc. of butter				Total samples tested
	0	1–10	11–100	Over 100	
A	21	1	0	0	22
B	18	4	0	0	22
C	14	4	0	0	18
D	11	7	0	0	18
E	10	6	0	0	16
F	6	6	2	2	16
G	6	11	4	1	22
H	6	6	3	7	22
I	0	5	0	9	14

Creamery A achieved an enviable record during 1932. One colony developed from one sample; all others tested were found to be free from both molds and yeasts. During the years 1930 and 1931 this creamery did even better: no fungi were found in any of the 22 samples analyzed each year. This creamery has demonstrated that butter can be produced commercially without molds or yeasts.

On the basis of mold counts, creameries B and E are good, F and G fair and H and I poor.

Several Manitoba creameries have been able to produce butter relatively free from molds by exercising great care in all stages of the manufacturing process. This accomplishment may be attributed to stimulation of effort resulting from: direct supervision by the Provincial and Federal Dairy Branches; Dairy School instruction; systematic laboratory analyses of butter; the inclusion of mold and yeast counts in the official score card for exhibition butter; and prizes awarded for the lowest counts of fungi during the season.

The value of care in every detail of manufacture is indicated in Table III, obtained by comparing the results achieved by creameries providing special

TABLE III

MOLDS IN SPECIAL AND COMMERCIAL BUTTER

Type of butter	Number of samples	Per cent of samples in classes of molds per cc.			
		0	1–10	11–100	Over 100
Special	146	41.8	47.4	9.5	1.3
Commercial	404	32.4	44.3	17.6	5.7

competitive samples as well as regular commercial butter*. The competitive samples had significantly fewer fungi.

**The writers are grateful to Professor N. James, of the Bacteriology Department, for much assistance, and to the staffs of the Provincial and Federal Dairy Branches, for taking the samples.*

The Groups of Fungi Found in Butter

All Phycomycetes isolated belonged to the Mucorales. Only six cultures (1%) were found in this group, whereas 5% of the soil fungi were Mucorales (1). All the five species isolated from butter are known to occur in soil.

Ascomycetes were found twice only: the *Chaetomium* probably developed in nature on manure, the *Valsa* on a twig.

Basidiomycetes might enter the creamery as spores carried in the air, but only one culture was recognized as belonging to this class of fungi.

The Fungi Imperfecti constituted nearly 99% of the isolations. Various *Penicillia* appeared, this genus being represented by 17% of the total number of isolations. Dr. Thom kindly examined cultures of the various species. There seems to be little evidence that certain forms of *Penicillium* should be considered as characteristic of butter; the species most common in butter are common in soil also. It is curious, however, that *P. intricatum* and *P. janthinellum*, found to be two of the commonest soil *Penicillia* in Manitoba, did not appear in butter. The writers are glad to acknowledge Dr. Thom's help with species of *Aspergillus* and *Paecilomyces* also.

Oospora lactis (Oidium lactis) and *Mycoderma* spp. were exceedingly common in butter. Relatively few of these fungi were transferred from the plates to the 614 test tubes which were studied.

Alternaria and *Cladosporium* are two dark-spored genera (Dematiaceae) commonly found in butter, which may be particularly objectionable because of the dark colonies produced.

Fusaria occasionally developed in cultures. Dr. W. L. Gordon kindly identified the four species which appeared.

Most of the other Imperfecti are common molds. *Phoma hibernica*, however, constitutes an unsolved mystery.

List of Species Isolated

The numbers in parentheses following the scientific names of the fungi refer to the numbers of times the species appeared in the isolations studied. These numbers represent roughly the relative frequency of the various species isolated, except that yeasts, which are very common in butter, were not isolated, and *Oospora lactis* and *Mycoderma* spp., which were also very common, were not transferred to test tubes in proportion to their prevalence.

When a remark is included within the parenthesis regarding the occurrence of a fungus in soil or elsewhere, it is to be understood always that soil (see 1) or other strata in Manitoba is meant. Very brief notes are given regarding certain species of fungi.

Absidia spinosa Lendner (1, occasional also in soil).

Alternaria tenuis Nees group (5, also in soil).

Alternaria spp. (59, common in soil and on old parts of plants). The dark growth produced by *Alternaria* is particularly objectionable in butter.

Aspergillus flavipes (Bain. and Sart.) Thom and Church (3, common in soil).

Aspergillus flavus Link (5, also in soil).

Aspergillus fumigatus Fres. (4, occurs in soil and on debris).

Aspergillus niger van Tieg. (3, not found to be common in soil or on plant parts).

Aspergillus terreus Thom (2).

Aspergillus ustus (Bain.) Thom. and Church (1, occasional in soil).

Aspergillus sp., perhaps ***nidulans*** group (2). Perithecia with purplish ascospores are produced in culture.

Basidiomycete. One culture produces white mycelium with clamp connections, but no spores. One or two other cultures may possibly be Basidiomycetes.

Botrytis cinerea Pers. (5, occurs on plants and in the soil).

Cephalosporium acremonium Corda (2, also in soil).

Chaetomium setosum Wint. (1). Setae first appear as lanceolate bristles, and later dichotomously branched hairs are found. Spores 6–8 × 4–5 μ.

Cladosporium herbarum (Pers.) Link (22, common on debris and in soil). Some of the forms may represent *C. butyri* Jensen, or possibly other species. *C. herbarum* is recorded (2) as generally present in molded butter.

Coniosporium arundinis (Corda) Sacc. (1, found once in soil).

Coniothyrium sp. (4, all from one sample). Spores greenish-brown, 4–8 × 3–4 μ.

Cunninghamella verticillata Paine (1). This distinctive fungus has oval spores mostly 10–14 μ long, covered with hair-like projections.

Diplodia sp. (1). Spores 14–16 × 6 μ, brown, two-celled.

Fusarium ?bulbigenum Cke. and Mass. (3).

Fusarium dimerum Penz. (3). Spores small, lunar with one or two cells.

Fusarium moniliforme Sheld. (4, also in soil).

Fusarium ?poae (Peck) Wollenw. (1, found in soil).

Geotrichum candidum Link (1, apparently identical with soil isolations).

Helminthosporium sativum Pam., King, and Bakke (1, common on cereals and in soil).

Hymenula affinis (Faut. and Lam.) Wollenw. (6, also in soil).

Monilia sitophila (Mont.) Sacc. (3, occasional in soil).

Mucor ?circinelloides van Tiegh. (2). Produces in culture a short turf, darkened with sporangia near the surface of the agar; the sporangiophores are branched, the spores 5–7 × 2½–3½ μ.

Mycoderma spp. (90 examined). Very common in butter. The cultures superficially resemble those of *Oospora lactis*. Both fungi doubtless indicate that the pasteurized cream had been recontaminated from unsanitary equipment with traces of raw cream or milk.

Oospora lactis (Fres.) Lindau (87 examined). Some variation occurs in cultures; the spores, or mycelial segments, are from 4 μ to 25 μ or longer; the cultures usually are whitish, but sometimes are pink. Other species of *Oospora* possibly may be included.

Paecilomyces aurea-cinnamomeum (Biourge) Thom (1 isolation obtained in 1931).

Paecilomyces varioti Bain. (22). This fungus, sometimes known as *Penicillium divaricatum*, is easily recognized by its spreading brown growth bearing penicillate heads with elliptical spores. Although common in butter, it has not yet been found elsewhere in Manitoba.

Penicillium atramentosum Thom (1, determined as apparently this species).

Penicillium aurantio-brunneum Dierckx (1, occasional in soil).

Penicillium brevi-compactum Dierckx (5). Strains show considerable variation.

Penicillium chrysogenum Thom (25, plus about 250 colonies from one sample badly contaminated with this species. Also very common in soil).

Penicillium ?cyclopium Westl. (2).

Penicillium expansum Link series (2).

Penicillium ?griseum Sopp. (as *Citromyces*; not *P. griseum* Bonord., 3 cultures).

Penicillium implicatum Biourge (1). Dr. Thom considers that this is a new variety characterized by the conspicuous development of transpired drops.

Penicillium johannioli Zaleski (2).

Penicillium lanosum Westl. (5).

Penicillium martensii Biourge (1).

Penicillium oxalicum Currie and Thom (2).

Penicillium purpurogenum Stoll (2, occasional in soil).

Penicillium ?purpurrescens Sopp (3, also in soil).

Penicillium restrictum Gilm. and Abb. (1, common in soil).

Penicillium roqueforti Thom (3). Strains of this species are used in making Roquefort cheese.

Penicillium rugulosum Thom (7, common in soil).

Penicillium sanguineum Sopp (1).

Penicillium spinulosum Thom (6, occasional in soil).

Penicillium terrestre Jensen (26, abundant in soil).

Penicillium viridicatum Westl. (1, also in soil).

Penicillium spp. (4 cultures not yet determined).

Phoma hibernica Grimes, O'Connor and Cummins (52). Abundant brownish pycnidia are produced, and masses of flesh-colored spores exude from them. The cultural characters agree with those described (7) for *P. hibernica*, although the spores in the Manitoba isolations are usually somewhat narrower, being 4–7 × 2–3 μ. This fungus, common in dairy products in Ireland and Manitoba, has not been found in or on other substrata. It was not encountered in an examination of several thousand fungi isolated from soil in Manitoba.

Phoma spp. (22). At least three species were found, one with spores 4 × 1 μ, another with spores 4–7 × 3 μ, and a third with spores 7–11 × 2–3μ. These *Phoma* stages no doubt represent contaminations from various plant sources.

Rhizopus elegans Eidam (1, frequent in soil).

Rhizopus nodosus Namysl (1).

Septoria sp. (7 from one sample). Spores curved, 18–24 × 1½–2 μ, in pycnidia.

Sporotrichum roseum Link (20, also in soil). Spores 3–6 × 2–3 μ.

Stemphylium sp. (1).

Torula spp. (3). As a rule yeasts were not isolated. However, some forms resembling molds proved to be *Torula*, possibly *Chromotorula*.

Trichoderma koningi Oud. (14, common in soil).

Trichoderma lignorum (Tode) Harz (16, common in soil and on old wood).

Valsa sp.? (1). Produces stromata with perithecia containing asci with allantoid spores 8–10 × 1½–2 μ.

Undetermined fungi (25.) Fourteen isolations did not produce spores on any of the media tried, and were finally discarded. Eleven other cultures are not yet named, although spores are present.

TABLE IV

SUMMARY OF FUNGI LISTED ABOVE

Class and genus	Number of entries	Number of isolations	Class and genus	Number of entries	Number of isolations
PHYCOMYCETES			FUNGI IMPERFECTI		
Absidia	1	1	*Geotrichum*	1	1
Cunninghamella	1	1	*Helminthosporium*	1	1
Mucor	1	2	*Hymenula*	1	6
Rhizopus	2	2	*Monilia*	1	3
			Mycoderma	1	90
ASCOMYCETES			*Oospora*	1	87
Chaetomium	1	1	*Paecilomyces*	2	23
Valsa	1	1	*Penicillium*	22	104
			Phoma	2	74
BASIDIOMYCETE	1	1	*Septoria*	1	7
			Sporotrichum	1	20
FUNGI IMPERFECTI			*Stemphylium*	1	1
Alternaria	2	64	*Torula*	1	3
Aspergillus	7	20	*Trichoderma*	2	30
Botrytis	1	5			
Cephalosporium	1	2	UNDETERMINED	—	25
Cladosporium	1	22			
Coniosporium	1	1			
Coniothyrium	1	4	Totals:		
Diplodia	1	1	29 genera	65 entries	614 cultures
Fusarium	4	11			

As a result of studies made on approximately 75 species of fungi isolated, 54 were specifically determined, 11 were placed in the genus only, and about 10 remain undetermined. Some species are included as doubtful. Nearly all the fungi isolated were saprophytes, although a few, as mentioned below, may have been parasites upon plants. Yeasts, *Oospora* and *Mycoderma*, were the commonest fungi found in butter, but *Penicillium*, *Phoma*, and *Alternaria* are common also.

Table V summarizes the molds recorded as found in butter by previous investigators and in this paper, and gives the probable or possible source of the molds.

It is noteworthy that of the 104 fungi entered below, only 3 are referred to in all three papers cited: these are *Alternaria* spp., *Cladosporium herbarum*, and *Oospora lactis*. *O. lactis* occurs in milk everywhere; the other two fungi are common molds on decaying parts of plants. It is probable that the fungi recorded as found in butter nearly all arise from spores or bits of mycelium from the soil, plants, debris, and manure; they are carried by the air or dust particles and contaminate the cream, equipment or butter. Most of the fungi found in butter produce spores abundantly.

TABLE V

FUNGI RECORDED IN BUTTER

Fungus	Recorded in			Probable habitat in nature	Fungus	Recorded in			Probable habitat in nature
	A*	B**	C†			A*	B**	C†	
Absidia spinosa			+	Soil§	*Mucor sylvaticus*	+			Soil
Acrostalagmus cinnabarinus		+		Plants††	*Mycoderma* spp.			+	Milk
Alternaria tenuis			+	Plants	*"Oidium variicolor"*	+			?
Alternaria spp.	+	+	+	Plants	*Oospora (Oidium) lactis*	+	+	+	Milk
Aspergillus flavipes			+	Soil	*Oospora ruberrima*	+			Debris
Aspergillus flavus	+		+	Plants, soil	*Paecilomyces aureo-cinnamomeum*			+	Debris
Aspergillus fumigatus		+	+	Plants, soil	*Paecilomyces varioti*			+	Debris, soil
Aspergillus glaucus	+	+		Plants	*Penicillium atramentosum*			+	Cheese ?
Aspergillus luteo-niger		+		Plants	*Penicillium aurantio-brunneum*			+	Soil
Aspergillus niger	+		+	Plants	*Penicillium brevi-compactum*		+	+	?
Aspergillus orysae	+			Plants	*Penicillium brevicaule*	+			Plants, soil
Aspergillus sydowi		+		Plants	*Penicillium chrysogenum*	+		+	Soil, debris
Aspergillus terreus		+	+	Soil, plants	*Penicillium crustaceum*	+			?
Aspergillus ustus			+	Soil	*Penicillium cyclopium*		+	+	Plants
Botrytis cinerea		+	+	Plants	*Penicillium expansum*	+		+	Plants, soil
Cephalosporium acremonium			+	Soil, fungi	*"Penicillium glaucum"*	+			?
Chaetomium bostrychoides	+			Manure	*Penicillium ?griseum*			+	Soil
Chaetomium setosum			+	Manure, debris	*Penicillium implicatum*			+	?
Cladosporium butyri	+			Milk ?	*Penicillium johannioli*		+	+	Plants
Cladosporium herbarum	+	+?	+	Plants, soil	*Penicillium lanosum*			+	Soil?
Coniosporium arundinis		+	+	Hay, soil	*Penicillium marlensii*			+	Plants
Coniothecium sp.	+			Plants	*"Penicillium ?olivaceum"*	+			?
Coniothyrium sp.			+	Plants	*Penicillium oxalicum*			+	Soil, plants
Cunninghamella verticillata			+	Soil	*Penicillium purpurogenum*			+	Soil
Dematium pullulans	+			Plants	*Penicillium ?purpurrescens*			+	Soil
Diplodia sp.			+	Plants	*Penicillium restrictum*			+	Soil
Epicoccum ?heterochroum (2)				?	*Penicillium roqueforti*	+		+	Milk?
Epicoccum sp.	+			Plants	*Penicillium rugulosum*			+	Soil
Eurotium repens	+			Plants	*Penicillium sanguineum*			+	Soil
Eurotium rubrum	+			Plants	*Penicillium sartoryi*		+		?
Fusarium ?bulbigenum			+	Plants	*Penicillium spinulosum*		+	+	Soil, plants
Fusarium dimerum			+	Plants	*Penicillium terrestre*			+	Soil
Fusarium moniliforme			+	Plants, soil	*Penicillium viridicatum*			+	Plants
Fusarium ?poae			+	Plants, soil	*Phoma hibernica* (see 7)		+	+	?
Fusarium reticulatum		+		Plants	*Phoma destructiva* (see 7)		+		Plants
Geotrichum candidum			+	Plants	*Rhizopus "arirus"*	+			
Gliocladium spp.		+		Plants, soil	*Rhizopus elegans*			+	Soil
Graphium penicilloides		+		Wood	*Rhizopus nodosus*			+	Soil
Helminthosporium sativum			+	Cereals	*Septoria* sp.			+	Plants
Hymenula affinis			+	Soil	*Sporotrichum carnis*		+		?
"Monilia alba"	+			Plants	*Sporotrichum roseum*			+	Soil
Monilia candida	+			Wood	*Stemyphylium butyri*	+			Milk?
Monilia sitophila			+	Debris, soil	*Stemphylium ericoctonum*		+		Plants
"Monilia rosea"	+			Debris	*Stemphylium* spp.		+	+	Plants
Mucor ? circinelloides			+	Soil, plants	*Stysanus microsporus*		+		Plants
Mucor corymbifer		+		Animals	*Torula* sp.		+	+	?
Mucor hiemalis	+			Soil	*Trichoderma koningi*			+	Soil
Mucor mucedo	+			Manure, soil	*Trichoderma lignorum*			+	Soil, wood
Mucor petrinsularis	+			?	*Trichosporium collae*	+			Debris
Mucor racemosus	+			Manure, soil	*Trichothecium roseum*		+		Plants
Mucor spinosus	+			Dung, debris	*Valsa* sp.			+	Plants
					Verticillium sp.	+			Plants

*A—Macy's summary (9). **B—Grimes et al (6). †C—This paper. §"Soil" fungi of course live for the most part on the remains of plants. ††"Plants" refers usually to old decaying plant parts.

It may be noted further that 32 or approximately half of the 65 fungi identified in Manitoba butter were isolated also from soil there (1). This indicates that soil, perhaps dust more particularly, is an important source of the fungi which find their way into cream or butter. During the dry summers such as have prevailed in recent years in western Canada, the total exclusion of dust particles requires extreme care.

Most of the fungi found in butter, including many of those occurring also in soil, develop more or less abundantly upon plants or plant parts, usually as saprophytes. A few species, such as those of *Fusarium*, *Helminthosporium*, *Diplodia*, *Septoria* and certain *Phomas*, are known to occur as parasites on plants. The spores of these fungi must be common in the air. A few fungi such as *Trichoderma lignorum* may develop upon wood in groves or the wood yard. *Oospora*, *Mycoderma* and yeasts multiply profusely in infected cream or milk.

Pasteurization of cream has been shown to be effective in killing the fungi present. The utmost vigilance is required to protect the product subsequent to pasteurization.

Inoculations upon Butter

Macy (9) and others have studied the growth of molds on various media, including sterile butter. The writers made a few tests of the more common fungi by inoculating them directly upon slices of salted and unsalted butter in Petri dishes. A good grade of creamery butter was used, which however already contained a few mold spores. When these slices of butter were inoculated and left for one to three weeks, scarcely any visible growth appeared upon them. Butter is rather low in moisture, and some evaporation from the Petri dishes occurs in the dry atmosphere of the laboratory. Accordingly 5 cc. of sterile water was added to each of a set of plates containing inoculated salted and unsalted butter. After a month, a small amount of growth from inoculations with *Alternaria* and *Oospora* only, appeared on the salted butter. Every plate of unsalted butter, however, showed conspicuous development of molds, to a considerable extent consisting of *Penicillia* and *Trichoderma* arising from contamination of the butter previous to inoculation. These few preliminary experiments suggest that low moisture content and the addition of salt are of value in restricting growth of molds, as found by Macy (10) and Voitkevich (13).

Discussion

It is exceedingly difficult, but not impossible, to exclude fungi from butter. Macy and Richie (11) and Grimes (5) found that the flavor and quality of fresh butter showed no correlation with the micro-organisms present (in a more or less dormant condition) in the samples. Macy and Richie (11) found, however, a tendency toward slightly better keeping quality when the yeast and mold counts were low. Certainly every effort should be made to minimize contamination of butter by foreign material; sanitary precautions automatically reduce the numbers of fungi in butter. Butter to

be shipped overseas, or otherwise held long in storage, should have the lowest possible count of fungi to start with, and should be kept at low temperature and low humidity. The addition of salt to butter lessens the development of molds.

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A PARASITOLOGICAL SURVEY OF THE GENUS *CITELLUS* IN MANITOBA[1]

By J. A. McLeod[2]

Abstract

A parasitological survey of 236 gophers (*Citellus* spp.) in the province of Manitoba yielded five previously recorded ectoparasites, four species of Nematodes, three of which are regarded as new to science, an Acanthocephalan and two previously unrecorded species of Cestodes. No Trematodes or intracellular Protozoa were found.

The importance of the Arthropod parasites as transmitters of disease, the pathogenicity of the enteric parasites and the correlation between the incidence of infestation and host abundance, are discussed.

Three species of *Citellus* commonly known as gophers are responsible for an immense annual loss to the farming industry of western Canada both in the destruction of growing crops and in the impeding of land cultivation by burrowing (6, 12, 14). There is also the possibility of such common rodents serving as alternate hosts, or as the direct carriers of organisms pathogenic to higher animals as do a number of closely related forms in other parts of the world (15, 22, 27).

It is well known that ground rodents are particularly susceptible to cyclic fluctuations of population density (3, 7, 8). Factors inducing such fluctuations are obscurely known but climatic extremes undoubtedly play a part. Overcrowding reduces the potential fertility. Bacterial and helminth parasitism may be pathogenic. Endemic helminth infestation may become epidemic under conditions of overcrowding or adverse climatic conditions with increased mortality and local fluctuations of population density as shown by Boughton (3).

Campaigns for the artificial control of these rodents by trapping, poisoning, burrow fumigation, etc., carried out at considerable expense in the past would appear to be unwarranted if epidemic disease regularly occurs when the population has reached a certain density. The presence of epidemic mortality among gophers is less easily detected than among non-burrowing forms and a continuous record of gopher abundance over the whole of Manitoba is not available. Such evidence as the writer has been able to collect from farmers and naturalists suggests strongly that there exist peak years of abundance followed by a sharp decline in population density. The peak years are not synchronous over the entire area but in the localities studied the maxima of abundance appear to be as follows:

C. tridecemlineatus.	1897–99	1912	1917	1923	1927	1932
C. franklini.		1912	1917	1923	1927	1932
C. richardsoni.		1912	1917	1923	1927	1932

[1] *Manuscript received June 8, 1933.*

Contribution from the Department of Zoology, University of Manitoba, Winnipeg, Manitoba, Canada. This paper was constructed from a thesis presented to the Committee on Postgraduate Studies, University of Manitoba, April, 1933, in part fulfilment of the requirements for the degree of M.Sc.

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The aim of the investigation reported below therefore has been that of surveying the parasitic fauna of the species of gophers present in Manitoba, with a view to ascertaining which members of that fauna have the potentiality of gopher destruction and which have the potentiality of spreading from gophers to man and higher animals in the capacity of disease vectors.

The survey included three species of *Citellus*. *C. franklini* and *C. tridecemlineatus* are indigenous forms representing 2 and 8% of the gopher population respectively, while *C. richardsoni* is an immigrant which came from the southwest about 1900 and represents about 90% of the gopher population (23, pp. 372–416). The report is based on the examination of 236 individuals from the southern half of Manitoba carried out during the period May to October, 1932, a year which appears to be a peak year of gopher abundance.

Methods

The animals examined during the survey were obtained from as many scattered points as possible for the purpose of comparing the incidence of each of the parasites in the different localities. As the area covered was approximately 80,000 square miles it was impossible to examine material from the different localities at regular intervals in an effort to determine the change of infestation with seasonal change and increase in the age of the host. Most of the animals were obtained alive, were etherized in the laboratory, the fur combed for ectoparasites, and a routine post-mortem examination performed.

The helminthological technique used was the standard technique recommended by other authors (26). Intestinal helminths were obtained by a decantation method, were washed in warm water and fixed in 70% alcohol at 75° C. (a method found satisfactory both for nematodes and cestodes) followed by preservation in 70% alcohol plus glycerol. Nematode preparations were made by clearing in glycerol-alcohol at room temperature and mounting in glycerol jelly. Cestode material was stained with Delafield's hematoxylin and cleared in beechwood creosote. This clearing agent was found most satisfactory also for the ectoparasitic fauna.

Taxonomy

The survey yielded five ectoparasites and seven endoparasites, which may be listed briefly as follows:

ARTHROPODA

Ixodidae.	*Dermacentor venustus*
Dermanyssidae.	*Liponyssus occidentalis*
	Liponyssus montanus
Pulicidae.	*Ceratophyllus bruneri*
Haematopinidae.	*Linognathoides montanus*

CESTODA

Dilepididae.	*Prochoanotaenia spermophili*, n. sp.
Hymenolepididae.	*Weinlandia citelli*, n. sp.

NEMATODA

Strongylidae.	*Warrenius bifurcatus*
Spiruridae.	*Rictularia citelli*, n. sp.
	Spirura infundibuliformis, n. sp.
	Physaloptera spinicauda, n. sp.

ACANTHOCEPHALA

Moniliformidae.	*Moniliformis spiradentatis*, n. sp.

The absence of Trematoda and of larval Cestoda is noteworthy, but it may be noted that Boughton (3) found no Trematoda and only two larval Cestoda.

All five species of ectoparasites were common to the three species of *Citellus* examined. Of the helminths, some were restricted to one *Citellus* species, others to two, and one occurred in all three host species as shown in Table I. The helminths were all found in the stomach or duodenum—the caecum, large intestine, liver, lungs and muscles being free from these parasites. About 40% of the gophers examined showed lesions of the stomach or intestine wall, but although a considerable number of such lesions were sectioned and examined no intracellular Protozoan was found. Several specimens showed splenic enlargement but time did not permit of the preparation and examination of blood smears of such individuals, and the writer was unaware at that time that a trypanosome had been recorded from *Citellus richardsoni*.

Table I is a record of the extent of infestation for each species of parasite for both young and adult of all three species of host. The young of *C. tridecemlineatus* and *C. franklini* were found to be uninfested up to the age of eight

TABLE I

THE RELATIVE INFESTATION OF THE THREE HOST SPECIES AND THE NUMBER OF PARASITES PER HOST

Parasite	Number examined	Per cent infested	Mean number of worms	Maximum number of worms
C. tridecemlineatus				
Rictularia citelli	71	21.1	4	8
Spirura infundibuliformis	71	19.4	18	48
Physaloptera spinicauda	71	15.4	2	4
Moniliformis spiradentatis	71	8.4	7	19
Weinlandia citelli	71	14	5	15
Prochoanotaenia spermophili	71	2.8	1	1
C. franklini				
Rictularia citelli	11	18.1	3	4
Physaloptera spinicauda	11	18.1	4	7
Weinlandia citelli	11	9	17	17
C. richardsoni				
Warrenius bifurcatus	154	62.0	24	83
Spirura infundibuliformis	154	0.6	2	3
Weinlandia citelli	154	2.9	8	20
Prochoanotaenia spermophili	154	1.9	8	17

weeks but those of *C. richardsoni* were heavily infested, in some cases at an early age. Females showed a slightly heavier infestation than males but this was not great enough to be of any particular significance. The mean and maximum number of parasites per host is of considerable importance however and will be discussed later.

Descriptions

Dermacentor venustus Banks, 1912

(*Dermacentor andersoni* Stiles, 1910)

Typical Ixodid ticks of medium-large size measuring up to 6 mm. in length in the adult.

Male. Has a well-developed scutum covering the entire dorsal surface of the body, which is chestnut brown with sparsely scattered white spots and unequal punctations. Scutum bears 13 festoons on the posterior margin. Mouth parts project forward beyond the anterior margin so as to be visible from the dorsal side. Eyes rather flat and at the sides, level with the second legs. The palps are much longer than broad and the second segment is without a retrograde spur. The spiracle is situated at the side of the body behind leg IV and the posterolateral extension of the peritreme is well developed.

Female. Scutum small and pale, being only slightly longer than broad and having the posterior border a little sinuous. The eyes, as in the male, are located at the sides, about the middle of the length of the scutum opposite the second pair of legs.

The species *venustus* is distinguished from the closely related species *occidentalis* and *albipictus* by the shape of the spiracle and the well-developed posterolateral extension of the peritreme.

Localities. Montana and Wyoming, U.S.A., Manitoba and British Columbia, Canada.

Ceratophyllus bruneri Baker, 1895

(*Ceratophyllus* Curtis, 1832)

Specific diagnosis. Siphonaptera of medium size with the three thoracic segments not strongly constricted and their epiphyses extending over but one abdominal segment. Abdominal tergites with two transverse rows of bristles. Pronotal comb with 18 ctenidia, genal comb absent and gena without recurved process. Head bluntly rounded anteriorly. Eyes present, genal row with one bristle. Labial palps with four pseudojoints and reach to about the distal end of the femora. Maxillary palpi shorter than the anterior coxa. Legs slender.

Female. Third joint of the antenna with nine pseudojoints distinct on the posterior side, but indistinct on the anterior. Second joint of the antenna with a row of fine hairs which extend almost to the distal end of joint III. Gena without recurved process but style present. Three antipygidial bristles present.

Male. Body slightly smaller than female and with the posterior end curved dorsally. Third joint of antenna distinctly divided into nine pseudojoints. Gena without recurved process, style absent. Three antipygidial bristles, claspers short, smooth on the ventral margin, and bristles are in a small group of five near the upper end.

Host and locality. *Citellus* sp. Montana; *C. tridecemlineatus*, *C. franklini* and *C. richardsoni*, Manitoba.

Liponyssus occidentalis Ewing, 1923

(*Liponyssus* Kolenati, 1859)

Female. Small with large dorsal shield. Palpi moderate, chelicera stout. Dorsal shield extending across the body at the shoulders, lateral margins behind the shoulders convex. Peritreme long and very sinuous, reaching to the anterior coxa. Sternal plate about three times as broad as long, barely reaching to the third coxa, and with the anterior margin strongly arched. Anterior setae situated on the anterior margin; middle setae situated on a line between the anterior and posterior setae, the latter being almost at the tip of the posterior angles. Anal plate egg-shaped in outline; anus small, almost circular with a uniform rim and situated in front of the middle transverse line; paired setae situated near the level of the anterior margin of the anus. Posterior setae situated more than their length behind the anus; caudal area forming a lobe-like projection of the anal plate. Legs moderate. Body length 0.61 mm., width about 0.31 mm.

Male. Unknown.

Hosts. *C. richardsoni* and *C. tridecemlineatus*.

Locality. Montana and Manitoba.

Liponyssus montanus Ewing, 1923

Female. Large, the body length being about 1.02 mm. and the width about 0.60 mm. Palpi large; chelicera shear-like but the hooked tips of both arms are rather blunt. Dorsal shield medium, lateral margins behind the shoulders very slightly convex. Peritreme long and sinuous and extending to opposite coxa I. Sternal plate with posterior corners broadly rounded and not extended. Anal plate very large, broadly rounded in front and somewhat truncate behind; anus subcircular with a uniform rim, and situated almost centrally; paired setae situated far forward, being at the level of the anterior margin of the anus; median seta situated about its length behind the anus; caudal area crescentic, scobiate. Legs long, anterior pair longer than the second pair and about equal to the third pair. Last pair reaching to about the tip of the abdomen.

Male. Unknown.

Host. *C. richardsoni* and *C. tridecemlineatus*.

Locality. Montana and Manitoba.

Linognathoides montanus Osborn, 1912

(*Linognathoides* Cummings, 1914)

Specific diagnosis. First pair of legs smaller than either the second or third pair. Abdominal pleural plates rudimentary. Six pairs of abdominal spiracles present opening on the flat body surface. Abdomen clothed with normal setae with never more than a single transverse row on a typical segment. Antennae five segmented, the second being the longest and the last two being distinct. Temples slightly swollen but without posterolateral angles.

Male. Body about 0.84 mm. long and about 0.4 mm. in greatest body width. Head about the size of the thorax; temples swollen; clypeal region pointed, forehead knob-like. Legs stout with well-developed single claws on the tarsi of the first pair. Posterior end broadly rounded. Color, light brown.

Female. Body length about 1.15 mm. by about 0.4 mm. in greatest body width. Head antennae and legs similar in size and shape to those of the male. Abdomen large and rectangular, ending bluntly. Body color, dark brown.

Host. Species of *Citellus.*

Locality. Practically all over the North American continent.

Warrenius bifurcatus Hall, 1916

Generic diagnosis. Head simple, no lips evident. Bursa is deeply incised dorsally to form two large lateral lobes and a small dorsal lobe. The dorsal, lateral and ventral ray systems are well defined and separated from one another, the rays of each system being more closely related to one another than to the rays of the other systems. The dorsal lobe is supported by the dorsal ray which branches dichotomously. The spicules are well developed, uteri divergent, vulva in the posterior half of the body, ovijector well developed.

Specific diagnosis. The worms are whitish in color after fixation but the intestines are red in living specimens. Cuticle is finely striated transversely and presents also about 24 longitudinal striae running the full length of the body. The nerve ring is situated about one-third of the way along the esophagus from the anterior end of the body. The esophagus is dilated posteriorly and separated from the mesenteron by a constriction. The excretory pore is about two-thirds of the way along the esophagus.

Male. Length 7–12 mm. Greatest body width 215 μ. Diameter of head exclusive of cuticular inflation about 36 μ. Length of the esophagus about 600 μ. Right spicule is bifurcated in a horizontal plane, left in a vertical. Right lobe of the bursa is about one and one-half times as long as the left.

Female. Length 15–18 mm. Greatest body width 315–335 μ. Diameter of head exclusive of cuticular inflation about 48 μ. Length of esophagus about 750 μ. Distance of the anus from the posterior end ranges from 88 to 120 μ. The vulva is a transverse crescentic slit about 2.6 mm. from the posterior end which bears a minute curved cuticular spine.

Eggs. Very numerous in gravid females; 12–16 segmented and enclosed in a thin shell.

Host. *C. richardsoni*, in stomach and duodenum.

Locality. Manitoba and Saskatchewan, Canada.
This species has been fully described by Sleggs (24).

Rictularia citelli n. sp.

(Figs. 1, 2, 3, 4)

Specific diagnosis. Buccal capsule well developed and narrow with its aperture more or less distinctly dorsal and with its base armed with teeth and spines. Along practically the entire ventral surface on each side there is a row of cuticular spines. Vulva anterior, near the posterior end of the esophagus. Oviparous, the eggs containing well-developed embryos when oviposited.

Female. Rather stout worms measuring from 30 to 60 mm. in length; of a pinkish color when alive but turning almost white on fixation. The following body measurements were found to be constant for gravid females 44 mm. in length. The head including cuticle is 235 μ in diameter and the body increases in thickness gradually until at a point one-fifth of its length from the posterior end it is 910 μ in diameter. This diameter is held or only slightly reduced to a point a short distance from the caudal end where attenuation takes place sharply, the body ending in a sharp point. Cuticle is about 12 μ thick in the head region and is definitely annulated along the neck. There is a pair of stout lateral cervical papillae about 630 μ from the anterior end. The first cuticular spine in each row is situated posteriorly and slightly ventrally to the mouth, there being 28 spines in each row from the head region to the vulva. Mouth is reniform in shape and is bounded by two subequal lips. The dorsal lip bears a short conical tooth on each side of its apex while the ventral one is smooth, semicircular and forms the helmet-like anterior termination of the body. The esophagus is simple, slightly dilated in the middle region and ends posteriorly in a hemispherical projection into the intestine. The vulva is a short transverse slit near the posterior end of the esophagus and is bounded by prominent lips formed of cuticle overlying finger-like projections of the body wall. The body is slightly expanded on each side of the vulva. The vagina is long and bifurcates posteriorly to form two convergent uteri which terminate in filiform ovaries.

Eggs. The eggs are 47–52 μ in length by 34–38 μ in width, very numerous, elliptical in shape with thick shells and each contains a coiled larva.

Male. Like many of the species of this genus, the males of *Rictularia citelli* are rare, there being only a single male found in the 50 specimens examined. This specimen, measuring 14 mm. in length, resembled the female in body shape, presence of cervical papillae, mouth structures and cuticular annulations. There were 28 combs in each row from the head region to the transition

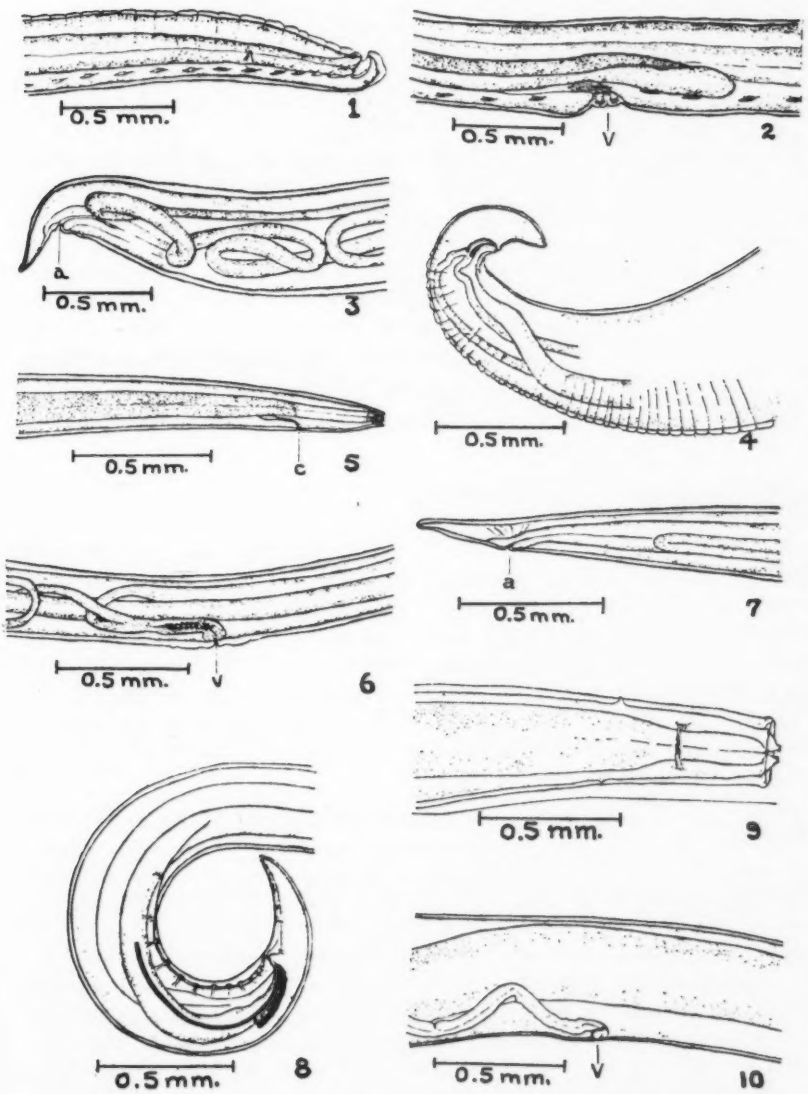


FIG. 1. *Rictularia citelli. Anterior extremity, lateral view.* FIG. 2. *Rictularia citelli. Body in region of vulva. V, vulva.* FIG. 3. *Rictularia citelli. Female, posterior extremity, lateral view. a, anus.* FIG. 4. *Rictularia citelli. Male, posterior extremity, lateral view.* FIG. 5. *Spirura infundibuliformis. Anterior extremity, lateral view. C, cervical pore.* FIG. 6. *Spirura infundibuliformis. Body in region of vulva. V, vulva.* FIG. 7. *Spirura infundibuliformis. Female, posterior extremity, lateral view. a, anus.* FIG. 8. *Spirura infundibuliformis. Male, posterior extremity, lateral view.* FIG. 9. *Physaloptera spinicauda. Anterior extremity, dorsal view.* FIG. 10. *Physaloptera spinicauda. Body in region of vulva. V, vulva.*

point, posterior to which the rows of combs extended almost to the caudal end. The posterior end of the body is obtusely conical, ending in a blunt point and is sharply curved ventrally. The anus is situated on a slight elevation 227 μ from the end of the tail. The spicules are equal, small and curved, measuring 117 μ in length. A gubernaculum is absent.

The possession of two lips and a definite buccal cavity along with a short muscular and a long glandular region of the esophagus, simple intestine and vulva opening in the midbody region, places this nematode in the superfamily Spiruroidea. The absence of projecting processes on the head and the presence of two longitudinal rows of spines on the ventral surface identifies it as a member of the genus *Rictularia*. The shape and position of the cervical papillae and the number of cuticular spines between the head region and the transition point serve to distinguish this from other species and is considered sufficient grounds for the creation of a new species.

Type host. *C. tridecemlineatus* and *C. franklini* (in stomach and duodenum).

Type locality. Manitoba, Canada.

Spirura infundibuliformis n. sp.

(Figs. 5, 6, 7, 8)

Specific diagnosis. Posterior portion of the body decidedly thicker than the anterior portion. Cuticle densely striated transversely. At a distance one-seventh to one-twelfth of the total body length from the anterior end is a prominent cuticular boss or struma. The anterior end is bluntly rounded. Mouth with two inconspicuous lips each bearing three papillae and surrounded by chitinous projections of the vestibule. Vestibule well marked, wide and cylindrical when seen laterally. Esophagus narrow and cylindrical, one-sixth as long as the body.

Male. Length 28 to 34 mm. with a gradual increase in body width from the narrow head to a point just anterior to the tail. Body widths for specimens measuring 31 mm. in length are as follows:—head 79 μ, mid-cervical region 210 μ, posterior to boss 253 μ, and posterior region 367 μ. The mouth width is 43 μ and the length of the vestibule 87 μ. Cervical pore opens 402 μ from the anterior end and the boss is situated 2.4 mm. from the anterior end. The esophagus is narrow, about one-sixth as long as the body and is divided into an anterior muscular portion reaching posterior to the cervical pore, and a long glandular posterior portion. The anterior end of the body is bent ventrally at an angle of 45° just posterior to the boss. The caudal end is sharply coiled ventrally. Two curved very unequal spicules are present, the right being 770 μ in length while the left is 297 μ. A gubernaculum is present. The caudal end bears two long narrow alae which meet behind at the tip of the tail but do not meet on the ventral side anterior to the anus. These alae are supported by twelve pairs of pedunculated pre-anal papillae and six pairs of short post-anal papillae, the last two pairs of which are close to the posterior extremity.

Female. Length 20–41 mm., and decidedly thicker near the posterior end. The diameters of specimens 40 mm. long are as follows:—head 96 μ, anterior end of esophagus 175 μ, behind struma 437 μ, mid-body and posterior regions 542 μ. The esophagus is one-sixth as long as the body and the boss is situated 2.17 mm. from the anterior end. The posterior end of the body is straight and conical with an obtuse termination. The anus opens 420 μ from the posterior end. The vulva is situated on the ventral side about five-eighths of the body length from the anterior end and is a prominent transverse slit with conspicuous lips, the cuticle being slightly thickened for a distance on each side of the aperture. There is a short vagina connecting with an infundibuliform ovijector which has a chitinous lining inside the muscular wall. This chitinous lining is thrown up into folds forming oblique valves on the wall with their free ends directed toward the vagina. The short common trunk of the uterus divides to form two divergent uteri.

Eggs. Roundly elliptical in shape and have thick smooth shells. They are very numerous in gravid females and measure from 36 to 39 μ in length by 27 to 30 μ in breadth.

The identity of this nematode as a member of the superfamily Spiruroidea is established by the possession of two indefinite simple lips, definite vestibule and long esophagus followed by a simple intestine, and the opening of the vulva near the middle of the body. The presence of a cuticular boss and a definite nerve ring together with well-developed caudal alae in the male supported by costiform papillae places it in the genus *Spirura*. This species resembles to a great extent the species *Spirura talpae* Gmelin, 1790. The females differ in body size, the number and size of the eggs produced and in the posterior body termination. This species terminates in an obtuse cone, the concave surface posterior to the anus, so pronounced in the species *Spirura talpae*, being absent. Apart from body size the males differ only in the number of papillae supporting the caudal alae. This species has twelve pairs of pre-anal and six pairs of post-anal papillae, while the species *talpae* has four pairs of pre-anal and five pairs of post-anal papillae (13).

In the opinion of the writer the nematode described represents a hitherto unrecorded species and the specific name *infundibuliformis* is suggested.

Type host. *C. tridecemlineatus* and *C. richardsoni* (in stomach and duodenum).

Type locality. Manitoba, Canada.

Physaloptera spinicauda, n. sp.

(Figs. 9, 10, 11, 12)

Specific diagnosis. Large relatively thick worms with two large simple triangular lateral lips each armed with two teeth and bearing a papilla at its apex. Cuticle may be reflected over the head to form a cephalic collarette or may be retracted and thrown into folds in the anterior cervical region.

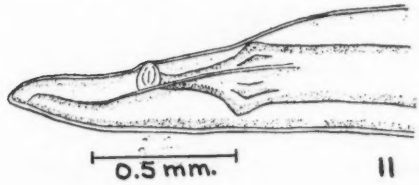
Cervical papillae posterior to the nerve ring; buccal cavity is short and a definite vestibule is absent. Esophagus divided into a short muscular anterior part and a long glandular posterior part. Cuticle densely striated transversely.

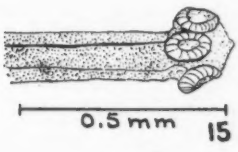
Male. Length from 15 to 20 mm., the body being slightly attenuated at the anterior end. Head round, continuous with the body and with two triangular lateral lips each of which terminates in a short papilla. Each lip bears two short teeth on its inner surface near the base of the papilla. In specimens 18 mm. in length the cuticle was thrown up so as to form a cephalic collarette 52 μ in length and 280 μ in diameter. The head was 210 μ wide with a shallow buccal cavity but a vestibule was absent. Two lateral cervical papillae are present about 700 μ from the anterior end, the left being slightly posterior to the other. The esophagus is broad and about one-fifth as long as the body, the anterior one-sixth being muscular and the remainder being glandular. A distinct nerve ring is present about 437 μ from the anterior end. The body is cylindrical and of uniform thickness being about 612 μ. The caudal end is conical and flattened on the ventral side, ending in a blunt point and is curved ventrally. The large caudal alae which meet anteriorly are supported by four long costiform papillae, two pre-anal and two post-anal. A single sessile median papilla is present about 245 μ from the posterior body termination. A gubernaculum is absent and the two sub-equal spicules measure 437 μ and 700 μ. The anus is situated on an elevation 875 μ from the posterior end and the curved ventral surface of the caudal region bears numerous longitudinal rows of very fine cuticular projections.

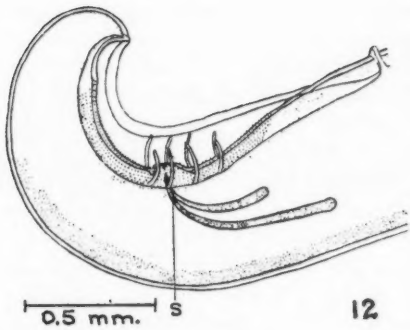
Female. Length from 18 to 50 mm. Generally resemble the male with regard to body shape and head structures. Cuticle is very dense and transversely striated. The vulva is a very small inconspicuous circular opening at the end of the anterior one-third of the body. There is a narrow tubular vagina of considerable length with a sphincter muscle at its outer end. The two divergent uteri lie as much-coiled tubes posterior to the vulva in the non-gravid female but in the gravid female the anterior uterus reaches to within a short distance of the esophagus. The tail is acute and ends bluntly, being flattened dorsoventrally. The anus is situated on a prominent elevation and the intestine is large.

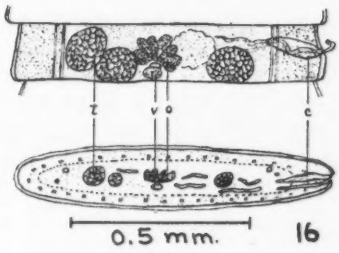
Eggs. Roundly elliptical, measuring 41 μ to 44 μ in length by 28 μ to 32 μ in breadth. They are thick shelled and very numerous.

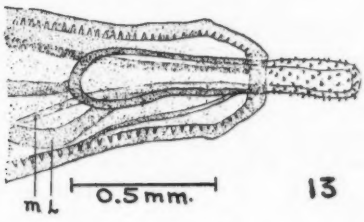
The presence of two large triangular lateral lips and a cephalic collarette and absence of a vestibule, together with large caudal alae supported by long costiform papillae in the males of this species, is considered sufficient reason for placing it in the genus *Physaloptera* of the superfamily Spiruroidea. It differs however from *P. citelli*, the only recorded species from *Citellus*, in general body size and in the possession of only two head papillae. This is considered sufficient grounds for the creation of a new species for which the name ***spinicauda*** is suggested.

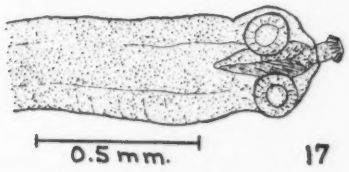


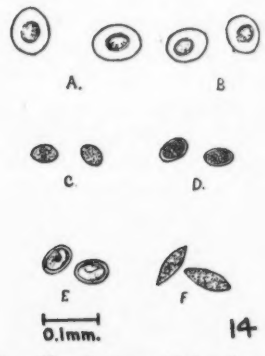












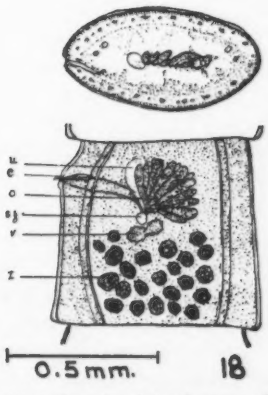


FIG. 11. *Physaloptera spinicauda. Female, posterior extremity, lateral view.* FIG. 12. *Physaloptera spinicauda. Male, posterior extremity, lateral view. S, spicules.* FIG. 13. *Moniliformis spiradentatis. Anterior extremity, dorsal view. m, muscles; L, limnisci.* FIG. 14. *Eggs. A, Weinlandia; B, Prochoanotaenia spermophili; C, Physaloptera spinicauda; D, Spirura infundibuliformis; E, Rictularia citelli; F, Moniliformis spiradentatis.* FIG. 15. *Weinlandia citelli. Scolex and neck, ventro-lateral view.* FIG. 16. *Weinlandia citelli. Proglottis. t, testes; v, vitellarium; o, ovary; c, cirrus sac.* FIG. 17. *Prochoanotaenia spermophili. Scolex and neck, dorsal view.* FIG. 18. *Prochoanotaenia spermophili. Proglottis. u, ulerus; c, cirrus sac; o, ovary; sg, shell gland; v, vitellarium; t, testes.*

Type host. *C. tridecemlineatus* and *C. franklini* (in stomach and duodenum).

Type locality. Manitoba, Canada.

Moniliformis spiradentatis n. sp.

(Fig. 13)

Specific diagnosis. Echinorhinchidea of medium to large size. Body without spines and is divided into a large number of pseudo-segments. Neck absent, proboscis well developed subcylindrical and armed with numerous rows of hooks which are small and have only a single posteriorly directed root. Limnisci filiform, with numerous nuclei. Testes ellipsoidal and situated quite posteriorly; prostatic glands eight, compressed and almost spherical.

These worms are very variable in size even from a single host, the males ranging in length from 35 to 110 mm., while the females range from 45 to 190 mm. The body widths also vary greatly being from 0.73 mm. in the smallest males and females to 1.2 mm. and 2 mm. respectively for the larger specimens. In fully developed worms the body is somewhat flattened and except at the two extremities is marked out into a large number of pseudo-segments; the posterior end is considerably broader than the anterior in large specimens. The proboscis is relatively short, subcylindrical and with a broadly rounded end, the length being 0.40 to 0.42 mm. with a greatest breadth of about 0.16 mm. A short portion of the proximal end of the proboscis is bare but the remainder bears eight spirally arranged rows of hooks, there being 14–17 hooks in each row. Each hook is recurved, from 31–36 μ in length, and has but a single root. Proboscis receptacle is a double walled muscular sac with retractors passing through the posterior extremity. The outer wall of the receptacle is disposed in spiral bands.

The limnisci are narrow, contorted and about one-seventh as long as the body. The testes are situated posteriorly where they fill almost the entire body cavity, one being posterior to the other and close to it. Each testis is an elongated slightly curved body somewhat flattened dorsoventrally and measures from 1.3 to 1.6 mm. in length by 0.58 to 0.61 mm. in breadth. The prostatic glands are situated posterior to the testes very near the end of the body. They are eight in number and form an elongate group 0.8 to 0.84 mm. long and 0.35 to 0.38 mm. in greatest breadth.

Eggs are present in large numbers in small females 45 mm. long as well as the largest specimens. They are spindle-shaped with sharply rounded ends and measure 59 to 65 μ in length and 20 to 22 μ in width and have thin wrinkled shells when deposited. In younger females the shells are thicker and smooth giving the eggs a width of 26 to 28 μ. Eggs are only slightly segmented when deposited.

The above-described *Acanthocephala* possesses the characters of the genus *Moniliformis*, sub-order Echinorhinchidea. It resembles the species *Moniliformis moniliformis* (25) in general body shape and the arrangement of the various organs, but there are sufficient differences in the relative body measurements, the number and arrangement of the proboscid hooks and the shape

of the testes to warrant the creation of a new species, in the opinion of the writer, and the name *spiradentatis* is suggested.

Type host. C. tridecemlineatus (in stomach and intestine).

Type locality. Manitoba, Canada.

Weinlandia citelli, n. sp.

(Figs. 15, 16).

Type species. Weinlandia macrostrobilodes Mayhew, 1925. Length 15 cm. and greatest width 2.8 cm. The anterior portion is very much attenuated, the width just posterior to the scolex being 175 μ, while 27 cm. behind, where the sexual organs are first fully formed, it is 277 μ. Increase in width is gradual and the first gravid proglottid measures 1.3 mm. with a continuous increase toward the posterior end until a maximum width of 2.8 mm. is reached. There is scarcely any neck since the slight constrictions indicating the beginning of strobilization are evident about 180 μ behind the scolex. The length of an anterior proglottid is about one-eight of the width, but when the sex organs begin to develop there is an increase in length with regard to width so that at a point where they are 0.94 mm. wide the length of each proglottid is 157 μ. In the midbody region gravid segments of 1.57 mm. in width measure 330 μ in length. The genital pores are unilateral and on the right side.

The scolex is but little wider than the anterior end of the strobila and with the suckers measures 245 μ in width by 157 μ dorsoventrally. The suckers are elliptical and measure 113 μ in length and 87 μ in breadth with a prominent rim about 21 μ wide. The rostellum is a rather indefinite triangular structure at the anterior termination, about 38 μ long when extended.

Three testes are present, two lie at the posterior margin of the proglottid about equidistant from the ovary, one being poral and the other antiporal. The third is anterior and lateral to the posterior antiporal testis and may lie somewhat dorsal or ventral to it in some segments. The testes are oval or spherical in shape and in segments 930 μ in width measure 143 μ in length and 113 μ in width. The vas efferentia are very small tubes not readily discernible in *in toto* mounts but they appear to arise from the anterior margins of the testes. Those from the two antiporal testes unite to form a common duct which is joined by the one from the poral side. The cirrus sac is one of the most conspicuous structures of the proglottid and is a fusiform, slightly curved structure about 157 μ in length opening a little posterior to the middle of the proglottid on the right side.

The cirrus is a thin rod-like structure arising at the inner end of the cirrus sac and terminating in a clavate expansion which curves sharply anteriorly after passing through the opening.

The vagina is an indistinct, somewhat twisted tube which runs anteriorly from the shell gland for a short distance and then turns laterally passing with the vas deferens below the excretory vessels.

The ovary is deeply divided into eight oval or spherical lobes forming a crescent-shaped mass in the middle of the non-gravid proglottid. The vitelline gland is compact, almost spherical and lies in the concavity on the posterior side of the ovary, while the shell gland is also rounded and situated ventrally beneath the vitelline gland.

The uterus in the non-gravid proglottids is a small irregular sac situated anteriorly and to the left of the ovary. In gravid proglottids it extends almost to the edges of the segment, its margin being thrown into folds so deep in some places that a number of lobes are formed. There are two excretory vessels on each side of the strobila. They are narrow and almost straight tubes, the dorsal being slightly larger and median to the ventral. On the right side they pass close to the inner end of the cirrus sac.

Eggs oval to almost spherical in shape and measure 78–86 μ in length by 59–65 μ in width. There is a thin outer shell and thick albuminous layer about one-quarter of the diameter of the egg in thickness, surrounding the inner shell and hexacanth embryo.

The presence of three relatively large testes in each proglottid, sac-like uterus, unarmed rostellum and unilateral genital pores places the cestode described above in the family Hymenolepididae (Ariola, 1899) (18). The arrangement of the three testes, two being posterior and the third being anterior and lateral to the posterior antiporal testis supports the opinion that it is a member of the genus *Weinlandia* (Mayhew, 1925) (18). Twenty-seven species of this genus have been recorded from birds by Mayhew (18), but none from rodents of the genus *Citellus* as far as the writer is aware. There appears to be a definite host specificity among members of this family and it is considered unlikely that an avian species would be found in a mammal. The only Hymenolepid recorded from *Citellus* sp. to the author's knowledge is *H. megaloon* (Linstow, 1901) (16), which differs from the above species in the possession of a conical scolex with shallow bothria and three testes arranged in a posterior row. On these grounds it is considered as a hitherto unrecorded species and the specific name *citelli* is suggested.

Type host. C. tridecemlineatus, C. richardsoni, C. franklini (in stomach and intestine).

Type locality. Manitoba, Canada.

Prochoanotaenia spermophili, n. sp.

(Figs. 17, 18).

Small worms of not more than 10 cm. in length. The anterior end is somewhat attenuated but the increase in body width is gradual. Behind the scolex the body width is 334 μ, while in the midbody region sexually mature but non-gravid segments measure about 720 μ in greatest width. Gravid segments at the posterior end measure about 1 mm. in width. Distinct strobilization begins almost directly behind the scolex leaving a neck of only about 740 μ in length. The anterior proglottids are narrower at their

anterior ends, being about three-quarters of the width of the posterior ends, while the length is about two-thirds of the greatest width. In sexually mature but non-gravid segments the posterior width is about 710 μ, the anterior about 595 μ and the length about 635 μ. Gravid segments are about the same width at each end but are slightly expanded in the mid-region. Those with a width of 1.08 mm. have a length of about 1.45 mm. The genital pores are irregularly alternate usually in two's or three's.

The scolex is somewhat narrower than the neck and with the suckers measures about 332 μ in width and 227 μ in thickness. The suckers are on the dorsal and ventral surfaces and are prominent circular cups 122 μ in diameter with depressions 66 μ in diameter. The rostellum in a distended condition measured 105 μ in length and is a fungiform structure bearing on its expanded end a single circle of very fine hooks each with a single root. The rostellum is retractible into a dagger-shaped muscular bulb 315 μ in length and 105 μ in greatest width.

Testes are about 70 μ in diameter in proglottids 780 μ wide and are oval or spherical in shape. There are 20–25 in each proglottid and all are post-ovarial in position. The vas deferens is first discernible just anterior to the ovary where it runs anteriorly for a short distance and then follows a convoluted course laterally passing ventral to the excretory vessels to the cirrus sac. The cirrus sac is a fairly conspicuous clavate-shaped structure extending obliquely inward about 140 μ. In sexually mature segments it opens on a prominent lateral elevation about one-quarter of the length of the segment from the anterior end. The cirrus is convoluted and the blunt outer end projects through the opening in gravid segments.

The vagina is an indistinct arched tube running in an anterio-lateral direction. Its outer end is almost parallel to the cirrus sac and opens immediately posterior to it. Like the vas deferens it passes ventral to the longitudinal excretory canals.

The ovary is divided into 10 to 14 finger-like lobes radially arranged in a semicircle. It lies in the anterior half of the segment and is somewhat antiporal in position. The vitelline gland is a compact uni- or bilobed structure almost median in position and with an anterior angle or concavity close to which lies the spherical shell gland.

The uterus is an irregular sac anterior to the shell gland and dorsal to the ovary in sexually mature but non-gravid segments, but is replaced by egg capsules in the gravid ones. The excretory vessels run parallel to, and are about one-fifth of the width of the segment from the lateral margins.

Eggs. Very numerous in gravid segments and are 56–62 μ long by 42–46 μ wide. There is a thin smooth outer shell and a thick albuminous layer surrounding the inner shell and embryo which is 31–33 μ in diameter.

The possession of marginal genital pores, post-ovarial position of the vitelline gland, non T-shaped rostellar hooks and the post-ovarial arrangement of the testes identifies the above cestode as a member of the family Dile-

pididae. The presence of an unstable uterus which is replaced by egg capsules places it in the subfamily Dipylidinae. That it belongs to the genus *Prochoanotaenia* (19), is supported by the possession of a single set of genitalia, absence of spines on the neck, position of the genital ducts below the longitudinal excretory vessels, alternate genital pores and a rostellum with a single row of hooks. A search of the literature reveals the most closely related species from small mammalia to be *Taenia blanchardi* (20), recorded from *Talpa europaea*. This differs from the species described here in the armature of the rostellum, and the relative size of the suckers. *Taenia blanchardi* also differs in that the ovary is arranged around the vitellaria while in *Prochoanotaenia spermophili*, n. sp. the vitellaria lie posterior to the ovary. To the writer's knowledge no member of this genus has been recorded from *Citellus* and the name *spermophili* is suggested.

Type host. *C. tridecemlineatus*, *C. richardsoni.*

Type locality. Manitoba, Canada.

Discussion

Dermacentor venustus was found to be quite common in the adult stage on the majority of the *Citellus* species examined in the early summer. This tick plays an indispensable part in the transmission of *Pasteurella tularensis* and *Dermacentroxenos rickettsi* the causative organisms of tularemia and Rocky Mountain spotted fever (17, 22). These diseases have always been confined to regions where this tick is abundant since its host relations, feeding as it does during the early stages of its development on rodents which serve as reservoirs for the diseases and as adults on man and higher animals, makes it pre-eminently suited for the role it plays.

With a large gopher population as a potential reservoir and the widespread occurrence of such a potential transmitter as *Dermacentor venustus*, the outbreak of an epidemic would appear to depend only on the introduction of the virus in an infected animal or tick. *Dermacentor venustus* has also been responsible for a number of cases of tick paralysis (4).

Ceratophyllus bruneri was found to infest almost 100% of the gophers examined. No direct pathological condition results from the bite of this insect but bubonic and pneumonic plague of man, common in numerous parts of the world, owe their persistence to the presence of animal reservoirs in the form of small rodents and their transmission from one host to another to the fleas of these rodents (15). Climatic conditions in western Canada are sufficiently similar to those of the endemic plague areas to spread this disease if once introduced. *Ceratophyllus bruneri* may also act as the transmitter of *Trypanosoma citelli* and as the secondary host of the tapeworm *Weinlandia citelli.*

Warrenius bifurcatus ranks first as a pathogenic organism of all the parasites listed in this paper. It occurs in numbers up to 80 in a single host and is always found firmly attached with the anterior end deeply buried in the

sub-mucosa or circular muscle layer of the gut (Plate I, Fig. 1). They are blood feeders and tissue mutilators and their presence is always accompanied by a hemorrhagic and necrotic condition of the parts attacked. Chronic inflammation and sometimes perforation of the intestine results from the presence of these worms. It infests about 54% of the entire gopher population with a mean number of 24 worms per host, thus constituting a serious menace to the health of these rodents.

Spirura infundibuliformis is another tissue-mutilating form. It is found in large numbers attached through a loop of tissue at the cardiac end of the stomach, the struma preventing it from becoming dislodged. Large worms such as *Weinlandia citelli* and *Moniliformis spiradentatis* seriously interfere with the normal functioning of the intestine and may almost completely block it in some cases (Plate I, Fig. 2). In such a case the intestinal wall becomes stretched and thin with a general emaciated appearance.

Parasitism and Host Abundance

The effect of the environment on an animal species, such as weather conditions, food supply and associated organisms, may be manifest either directly in the longevity of the individual or indirectly in its fecundity. Members of the genus *Citellus*, due to their hibernating habit, are well adapted to withstand winter and other unfavorable weather conditions in western Canada unless interfered with from some other source. Since they live in what are now agricultural areas, food is very abundant during their active season and they are practically free from the attacks of such predators as the coyote, fox, badger, hawk and owl. It must rest then with pathogenic organisms to bring about the condition which so regularly depletes their numbers.

Parasitic infestation, as shown by Boughton (3), depends on the rate of egg production, life-cycle stages, presence of a secondary host where necessary and the chance of gaining entrance to the host. Overcrowding, resulting from rapid increase due to favorable weather and food conditions and the absence of predators, more than proportionately increases the possibility of the parasites gaining entrance to the host. Parasitic infestation also depends on the specific resistance of the host in a manner similar to bacterial infection (5). The detrimental influence of the Helminths listed in this paper is increased by the fact that they are metabiotic and several species can infest the host at the same time; in fact the greatest number of a single species was often found in the presence of other parasites. The presence of one species appears to lower the host's resistance and facilitate the existence of others. For example a single specimen of *C. tridecemlineatus* showed infestation as follows:—*Weinlandia citelli*, 8; *Moniliformis spiradentatis*, 19; *Spirura infundibuliformis*, 48; A single specimen of *C. richardsoni* also showed;—*Warrenius bifurcatus*, 62; *Weinlandia citelli*, 20; and *Prochoanotaenia spermophili*, 14.

Acknowledgments

This survey was carried out under the direction of Prof. R. A. Wardle to whom the author wishes to express his sincere thanks not only for permission to use his private literature files but also for many helpful suggestions, kind criticisms and for assistance in the preparation of the manuscript. Thanks are also due Mr. Stuart Criddle, Treesbank, Manitoba, and members of the Departments of Zoology and Biology, University of Manitoba, for valuable assistance.

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PLATE I

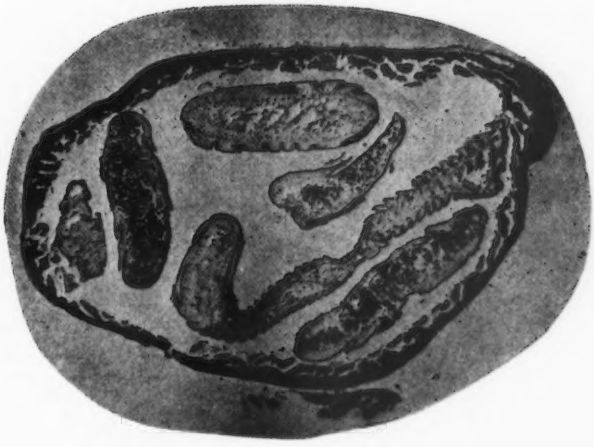

FIG. 1. *Transverse section of intestine with worms attached showing destruction of villi and inflamed sub-mucosa.* FIG. 2. *Transverse section of intestine with Weinlandia citelli in situ.*

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STUDIES ON BACILLUS CALMETTE-GUÉRIN (B.C.G.) AND VACCINATION AGAINST TUBERCULOSIS[1]

By E. A. Watson[2]

Abstract

Vaccination trials and biological studies of B.C.G. have been carried on for a period of over eight years and are still continuing. Under conditions of continuous exposure to natural infection through cohabitation with tuberculous animals, trials varying in duration from two months to four and one-half years have been completed on 44 vaccinated cattle and 28 unvaccinated controls. In trials of short duration the percentage of cattle free from tuberculosis is slightly in favor of the vaccinated. In all cattle over two years of age tuberculosis was present to a greater or lesser degree. Judged by slight, moderate and extensive tuberculous involvement, there is some evidence of a greater resistance in the vaccinated cattle up to two and a half years of age, 26% of which showed extensive generalized tuberculosis, as compared with 53% of the unvaccinated. But in the age group ranging from two and a half to four and a half years no greater resistance is found in the vaccinated than in the unvaccinated cattle. It has not been possible to demonstrate a true lasting immunity by this method of vaccination, and such increased relative resistance as B.C.G. may confer during the early months of life declines and soon disappears, and fails to protect cattle exposed for two years to natural sources of infection from developing typical tuberculosis.

The attenuated virulence and potential pathogenicity of B.C.G. have been studied for a period of over eight years in three original strains received in the years 1924, 1925 and 1927, and in the cultural descendants of each strain up to the year 1932. Each strain proved to possess an unfixed, potential virulence capable of exaltation on the one hand, and of complete attenuation or reduction on the other. This virulence, manifested but rarely and only in the earlier descendants, 1924-1928, declined under serial cultivation and periodic return to the special bile-potato media and apparently died out in the 1928-1929 generations, for none of the subsequent descendants tested proved capable of causing progressive reinoculable tuberculosis in laboratory animals.

A number of tuberculosis research studies engaged in by the Dominion Department of Agriculture were incorporated into the research program of this Associate Committee on Tuberculosis as drafted and adopted in the year 1925. These include studies relating to vaccination with living tubercle bacilli, and especially investigations of the claims made in respect to B.C.G. vaccination of cattle, begun more than eight years ago, and continuing under the direction of the writer and in collaboration with Drs. McIntosh and Konst up to the present time. Several interim reports have been made to this committee at previous meetings, and the present report is, more or less, a summary of (1) experimental trials of vaccination and resistance of cattle under exposure to natural sources of tuberculosis infection, and (2) experiments relating to the possible pathogenicity and virulence of B.C.G.

[1] *Manuscript received May 10, 1933.*

Contribution from the Animal Diseases Research Institute, Dominion Department of Agriculture, Hull, Quebec; presented at the seventh meeting of the Associate Committee on Tuberculosis, National Research Council, Ottawa, March 21, 1933.

[2] *Chief Pathologist, Animal Diseases Research Institute.*

Repetition of the Vaccination Experiments made by Calmette and Guérin, and the Determination of the Duration of the Immunity*

In reporting, interpreting, judging and evaluating the results of B.C.G. vaccination of cattle, careful consideration must be given to the conditions under which the vaccination and immunity trials are conducted and to which the animals are subject from the time of birth, and for the whole duration of the experiment. Apart from the variable degree of natural susceptibility and resistance in individual animals, many factors may enter, such as methods of handling calves at birth, of feeding and housing, and the environment in which the animals are placed; the sources of infection to which they are exposed, month by month, year by year; the severity, frequency and duration of those exposures; breeding, pregnancy and lactation, etc. Such conditions can be controlled only in part; and in practice will vary greatly from time to time and even from month to month, in degree and in kind, and have variable effect upon resistance and experimental results. A great deal of the conflicting results reported by different authors in different countries, or by the same author with different groups of animals spread over a period of years, is, in all probability, due in large measure to the different and varying conditions under which the trials are conducted, and to different prevailing factors. It appears, therefore, very necessary to state as clearly as possible the known conditions of the experiments and at the same time bear in mind that variable factors remain unknown. The cattle vaccination studies under the auspices of this committee have been made under conditions as here set forth:

1. The original cultures of B.C.G. were obtained direct from France, from Professors Calmette and Guérin. Subcultures were propagated successively on potato media and Sauton's special media, interrupted at each 10th to 12th generation by a return to ox-bile–potato media as recommended.

2. The vaccines injected into cattle were prepared from subcultures made under the conditions stated in paragraph No. 1. With each lot of prepared vaccine inoculated into cattle, pathogenicity tests were made on guinea pigs.

3. Each year, from 1925 to 1931, one or more groups of new-born calves were inoculated within the first few days of life with the prescribed dose of B.C.G., subcutaneously, in the dewlap.

4. Each year, from 1925 to 1931, one or more groups of calves have been left as controls, *i.e.*, unvaccinated, but otherwise subject to the same conditions as the vaccinated.

5. Calves born in the years 1925 and 1926 were vaccinated and exposed to infection without special safeguards or change in ordinary farm methods, and in accordance with the conditions prescribed at that time.

*(*Research Program, Associate Committee on Tuberculosis, Item 5 (d).*)

6. Calves born in the years 1927 to 1931 were strictly isolated and fed only pasteurized milk from birth, for a period of one to two months after vaccination with B.C.G., in accordance with the revised conditions laid down in 1927.

7. Vaccinated calves not disposed of during the first year of life were revaccinated, at intervals of approximately one year, until death or slaughter.

8. Exposure to infection was by natural means, first through the ingestion of raw milk from cows which included one or more tuberculous animals, and then by cohabitation with tuberculous cattle in stables and in pastures. In order to equalize hazards of exposure, the stable locations of the vaccinated, unvaccinated and tuberculous cattle were changed from time to time, and during the summer months the animals mingled together freely in small pastures or outside enclosures, in which they were fed from large open racks or mangers.

9. The duration of the exposure and immunity trials have varied from a few months up to four and a half years.

10. As a rule, the young males were first disposed of, within the first or second year of life, and later on the heifers after one or more periods of gestation and lactation.

11. Laboratory post-mortem examinations have been conducted in each case, and the search has been much more thorough than is customary or is possible under abattoir conditions.

12. Microscopical examinations and test inoculations have been made of the vaccinal nodes or lesions present in the dewlap, the lesions found in other tissues and organs, and of lymphatic gland tissues in which no visible lesions could be found.

The summaries and observations that follow concern only cattle in which the resistance or immunity has been tested by exposure to natural sources of infection under the conditions already stated.

In the above category there are 107 cattle, of which 35 are living and held for further trial and observation, and 72 are dead. The latter, consisting of 44 vaccinated cattle and 28 unvaccinated controls, died or were killed at an age ranging from two months to four and a half years and, in each case, were subject to necropsy under laboratory conditions, microscopical examinations and guinea pig test inoculations. Regardless of age or the duration of the trial, it was found that nine, or 20.5%, of the vaccinated, and six, or 21.4%, of the unvaccinated cattle were free from tuberculosis, and that tuberculosis was present in the remainder of each group.

The number and approximate percentage of cattle, according to (a) age grouping, and (b) cumulative results, are shown in Table I.

A slight difference in favor of the vaccinated cattle up to 18 months of age may be noted, but with accumulating numbers and results, and when

all cattle up to the age of four and a half years are included, the percentage is practically the same for the vaccinated and for the controls.

Actually, the cattle free from tuberculosis in both vaccinated and unvaccinated groups were under two years of age, and all cattle over two years of age showed tuberculosis to a greater or lesser degree.

TABLE I

VACCINATED AND UNVACCINATED CATTLE FREE FROM TUBERCULOSIS

Age groups	Number of cattle			Free from tuberculosis, %	
	B.C.G.	Controls	Total	B.C.G.	Controls
Up to 1 year	5	4	9	100	75
1 to 1½ years	8	3	11	25	0
1½ to 2 years	14	9	23	14	33
2 to 2½ years	9	4	13	0	0
2½ to 4½ years	8	8	16	0	0
All cattle	44	28	72	20	21
(*Cumulative*)					
Up to 1 year	5	4	9	100	75
Up to 1½ years	13	7	20	54	43
Up to 2 years	27	16	43	33	37
Up to 2½ years	36	20	56	25	30
Up to 4½ years	44	28	72	20	21

Comparative Resistance to Tuberculosis of Vaccinated and Unvaccinated Cattle

The comparative and relative resistance as indicated by the activities of tuberculous lesions and the extent of their involvement have been studied. Extreme variability in the type or stage, extent and location of the tuberculous processes is as noticeable in the vaccinated as in the unvaccinated groups, in each of which some animals show only small foci of infection limited to one or several groups of lymphatic glands; others have revealed more scattered lesions of a progressive type; and others, the classical picture of advanced generalized tuberculosis.

For convenience and to permit of a simple comparison, the degree and extent of tuberculosis is indicated in Table II by three subdivisions: slight, moderate, and extensive.

There is little difference in the incidence of tuberculosis in the vaccinated and unvaccinated groups, but there is some evidence that in the vaccinated cattle there is a greater degree of resistance up to two and a half years of age, and as indicated by 26% of the vaccinated and 53% of the unvaccinated with extensive involvement. It is noteworthy, however, that in the age group, two and a half to four and a half years, the percentage of cattle with slight, moderate and extensive tuberculosis, namely, 25, 25 and 50%, is identical for the vaccinated and unvaccinated cattle.

TABLE II

VACCINATED AND UNVACCINATED CATTLE WITH TUBERCULOUS INVOLVEMENT

Age group	Number of cattle		With tuberculosis, %			
			Slight	Moderate	Extensive	Total
Up to 1½ years	B.C.G.	13	38	8	0	46
	Controls	7	28	28	0	56
1½ to 2½ years	B.C.G.	23	30	35	26	91
	Controls	13	8	15	53	76
2½ to 4½ years	B.C.G.	8	25	25	50	100
	Controls	8	25	25	50	100
All cattle up to 4½ years	Totals:—					
	B.C.G.	44	32	25	22	79
	Controls	28	18	21	39	78

In brief, it may be said: (1) that in these groups of cattle, the greater degree of resistance of the B.C.G. vaccinated animals is best indicated in animals up to two to two and a half years of age; and (2) that the resistance in vaccinated animals which have reached breeding age, two and a half years and up, and after one or more periods of gestation and lactation, is more or less parallel or comparable with the resistance of unvaccinated cattle.

In other words, increased resistance following B.C.G. vaccination of newborn calves diminishes as the animals continue in cohabitation with tuberculous cattle and approach maturity, and is apparently lost in young cows which are being bred and milked.

There is evidence that B.C.G. vaccination causes or increases a relative resistance which may delay the development of infection and disease, particularly during the early period of life, but in most cases this is transient and declines as the animals approach maturity, and it has not been sustained by annual revaccination.

The results have varied considerably in individuals and in groups of animals which, of course, is to be expected in such a chronic disease as tuberculosis where the conditions of life and exposure to infection and reinfection on the one hand, and natural susceptibility and resistance on the other, are such variable and important factors.

One or two cases of more than usual interest may be mentioned. For example, a B.C.G. vaccinated animal, No. 188, was killed at the age of two years and ten months when in a moribund condition. During the last three months of life this animal showed increasing difficulty in breathing and swallowing, developed a very large swelling in the submaxilliary region, and became much emaciated. At necropsy, the retropharyngeal glands were uncovered as an enormous mass of caseo-purulent tuberculous lesions pressing upon the pharynx and larynx. There were no other visible lesions in the body except a small focus in the mesenteric gland.

Another B.C.G. vaccinated animal, No. 218, manifested clinical advanced tuberculosis and was moribund at two years and nine months of age. In addition to typical lesions of advanced pulmonary and lymphatic gland tuberculosis, the larynx and trachea showed extensive tuberculous ulcerations and caseo-purulent nodules. (See Plates I and II.)

The evidence thus far accumulated in the trials and experiments conducted over a period of seven to eight years, shows that approximately 80% of the cattle killed at ages ranging from calfhood to maturity developed tuberculosis to a variable extent while living under conditions of exposure to natural infection and reinfection, with approximately the same incidence in the vaccinated and in the unvaccinated, but at a slower rate of development and progress, especially in early life, in the vaccinated animals, thus indicating some increased resistance. This, possibly, would be more in evidence if and when B.C.G. vaccination is applied under conditions where exposure to infection is slight and infrequent and resistance is not weakened by the stress and strain to which breeding cattle, especially dairy cattle of high production, are subjected.

The Attenuated Virulence and Potential Pathogenicity of B.C.G.

Our experiments and studies relating to the attenuated virulence and the properties of B.C.G. have been made on the descendants of three original strains of B.C.G. received direct from France.

The first strain, herein referred to as B.C.G. 80, was forwarded by Dr. Guérin from the Pasteur Institute, Lille, and was received in November 1924.

The second strain, B.C.G. 17, came from Professor Calmette's laboratory, Pasteur Institute, Paris, September 1925.

The third strain, B.C.G. 346, also came from Calmette's laboratory, December 1927.

It is important, for several reasons, as will be seen later on, to keep in mind the fact that the work has been done with three parent strains and their descendants, the dates or years of their origin, 1924, 1925, 1927, and their succession and maintenance as separate B.C.G. strains up to the year 1932.

Tests of the descendants of these culture strains of B.C.G. have been spread over a period of eight years and have furnished an enormous number of data which are now being compiled in tabulated form and subjected to careful analysis. This analysis is bringing out features of special interest, some of which are presented in the following outline or summary.

1. Tests of 145 cultures of B.C.G., representative of subcultures descending to the 121st generation, have been made on over 500 guinea pigs.

In approximately 56% of the guinea pigs there was no evidence of tuberculosis at necropsy.

Slight or localized lesions, or apparently arrested or healed lesions, were present in 40% of the guinea pigs.

Typical tuberculosis, reinoculable from animal to animal, in series, or by reisolation in culture and subsequent inoculation, developed in 4% of the guinea pigs.

(Further reference to slight or arrested lesions may be omitted as such may, and probably do for the most part, fall into that category stressed by Calmette as undergoing healing, absorption and retrogression.

2. Only 6, or 4%, of the 145 B.C.G. cultures tested proved to be virulent for guinea pigs.

(It so happens, as a coincidence only, that the percentage of virulent cultures and the percentage of guinea pigs developing tuberculosis in all inoculation tests are the same, namely, 4%).

But 21, or 42%, of the 50 guinea pigs which received inoculations of these six virulent descendants, developed typical tuberculosis.

3. Each of these six virulent descendants proved to be capable of causing a progressive tuberculosis, reinoculable from animal to animal.

Four of these substrains of proved virulence were reisolated in culture, in the course of serial animal passage, and repeatedly proved pathogenic for guinea pigs and rabbits, and of a type and virulence corresponding to the usual bovine type.

4. The period in which these six virulent cultures were forthcoming dates from the end of the year 1924 to 1928, and for each parent or original strain is subdivided as follows:

(a) B.C.G. 80,—3 virulent descendants—1924 to 1926.

(b) B.C.G. 17,—2 virulent descendants—1925 to 1927.

(c) B.C.G. 346,—1 virulent descendant—1928.

None of the later descendants tested,—of B.C.G. 80 since 1926, of B.C.G. 17 since 1927, and of B.C.G. 346 since 1928,—proved to be virulent for guinea pigs or capable of causing a progressive, reinoculable tuberculosis.

5. Approximately 17% of test inoculations for virulence were positive in the year 1925; 10% in the years 1926 and 1927; less than 5% in the year 1928; and zero, or 0%, 1929-1932.

6. *B.C.G. strain 80*, the first strain received from France, 1924, has been tested at intervals between the 1st and 121st generation. Twenty-nine cultures, each of a different generation, were tested, and three, or 10.3%, proved virulent for 9.8% of the test guinea pigs. These three virulent cultures were produced between the 1st and 18th generation and no virulent cultures have since been produced from the 19th to the 121st generation.

B.C.G. strain 17, the second strain received from France, 1925, has been tested at intervals between the 14th and 107th generation. Seventy cultures were tested and two, or 2.8%, proved virulent for 2.4% of the test guinea pigs. These two virulent cultures represent the 22nd and 36th generation respectively, and no virulent culture has been produced in the succeeding 71 generations, *i.e.*, from the 37th to 107th generation.

B.C.G. strain 346, the third strain received from France, 1927, has been tested at intervals between the 13th and 77th generation. Forty-six cultures or descendants of different generations were tested and only one, or 2.1%, proved virulent for 0.64% of the test guinea pigs. This virulent culture represents the 13th generation, and all subsequent cultures up to the 77th generation have been negative.

7. The data and figures covering the entire eight-year period of culture and virulence testing show that the number and percentage of virulent subcultures derived from each parent strain, and also the number and percentage of positive inoculation tests, declined from the first year and had fallen to zero at the end of the fourth year (1924-1928) where it has remained for a further period of four years (1928-1932).

8. From the commencement, B.C.G. has been regularly and continuously reproduced in serial transfer upon the culture media, and in accordance with the procedure recommended by Calmette, being regularly returned to bile-potato media at stated intervals.

9. The virulence as determined in the small percentage of these early descendants (1924-1927) required a long period for its manifestation in the original test animal and, in some cases, did not reach full or average virulence until the second or third serial animal passage.

10. Experiments made to bring back or to restore the virulence lost by the B.C.G. descendants since 1928, by means of "dissociation" into different colony types, by "deep growth" methods of culture, by adding serum to the media, and in other ways, have not met with any certain success.

Conclusion

A careful analysis of the history of these strains of B.C.G. and of the virulence and pathogenicity tests of their descendants continuing over a period of eight years leads, in the opinion of the writer, to but one clear and certain conclusion:—that the Calmette-Guérin bacillus or "B.C.G.", as issued in the years 1924-1927, was still in process of attenuation, that its properties were not then completely and hereditarily fixed, and that it still retained a low, uncertain and potential virulence, which, in the one direction, by animal passages and reisolation has been exalted to and maintained at a high degree of virulence; and, in the other direction, in the course of several years of continuous culture and reproduction on the special laboratory media designed by the originators of B.C.G. for its attenuation, has declined and vanished.

It is surely significant that with cultures of B.C.G. that were being distributed for study in the years 1924-1927, not only the writer and his coworkers but a number of investigators in different countries reported experiments and evidence in disproof of the claim that B.C.G. was completely and absolutely devoid of virulence and that its properties were hereditarily fixed. Moreover, in 1927, Calmette recommended, as a safety precaution, that B.C.G. be returned to bile-potato at stated intervals.

It may here be recalled (Calmette and Guérin, Ann. inst. Pasteur, May, 1924) that B.C.G. originated from a highly virulent bovine strain of tubercle bacilli and that its virulence was slowly attenuated first for one species of susceptible animal and then for another, successively, during 13 years of cultivation on bile-potato, on which it apparently lost its property of tuberculin production, and since that date (January 5, 1921: 230th passage) was kept on ordinary glycerinated potato, "with the object of definitely fixing its properties"; and that under the latter conditions it regained its tuberculogenic properties.

It need occasion no surprise therefore, to discover that B.C.G. still retained some potential virulence, even though rarely manifested, and that this has been suppressed only by a continuation of the special cultural methods for its attenuation over a further period of years.

At this present time we can make the statement on positive proof evidence that the parent strains of B.C.G., as they came to us, and their early descendants possessed an unfixed potential virulence capable of exaltation on the one hand and of further and complete reduction on the other, each of which has been accomplished; and, on negative evidence, that the later descendants of the same strains (1929-1932), by continuous reproduction and periodic return to bile media in accordance with Calmette's recommended procedure, have become incapable of causing progressive, reinoculable tuberculosis in laboratory test animals.

EXPLANATION OF PLATES

Types of tuberculosis in cattle vaccinated with B.C.G. as newborn calves and raised in a tuberculous environment.

PLATE I

Fig. 1. Laryngeal and tracheal tuberculosis (No. 218).

PLATE II

Figs. 1 and 2. Pulmonary and hepatic tuberculosis (No. 218).

Figs. 3 and 4. Glandular tuberculosis (No. 188).

Animal No. 218. Born May 19, 1929. Isolated 40 days. B.C.G. vaccinations: May 27, 1929; June 28, 1930; June 29, 1931. Slaughtered March 1, 1932, at two years and 9 months of age. Large caseous retropharyngeal lymph nodes; caseo-purulent nodes and cavities in the lungs and liver, tuberculous ulceration of larynx and trachea.

Animal No. 188. Born July 4, 1928. Isolated 40 days. B.C.G. vaccinations: July 9, 1928; August 8, 1929; September 4, 1930. Slaughtered May 7, 1931, at two years and 10 months of age. Extensive tuberculosis of retropharnygeal lymph nodes.

PLATE I

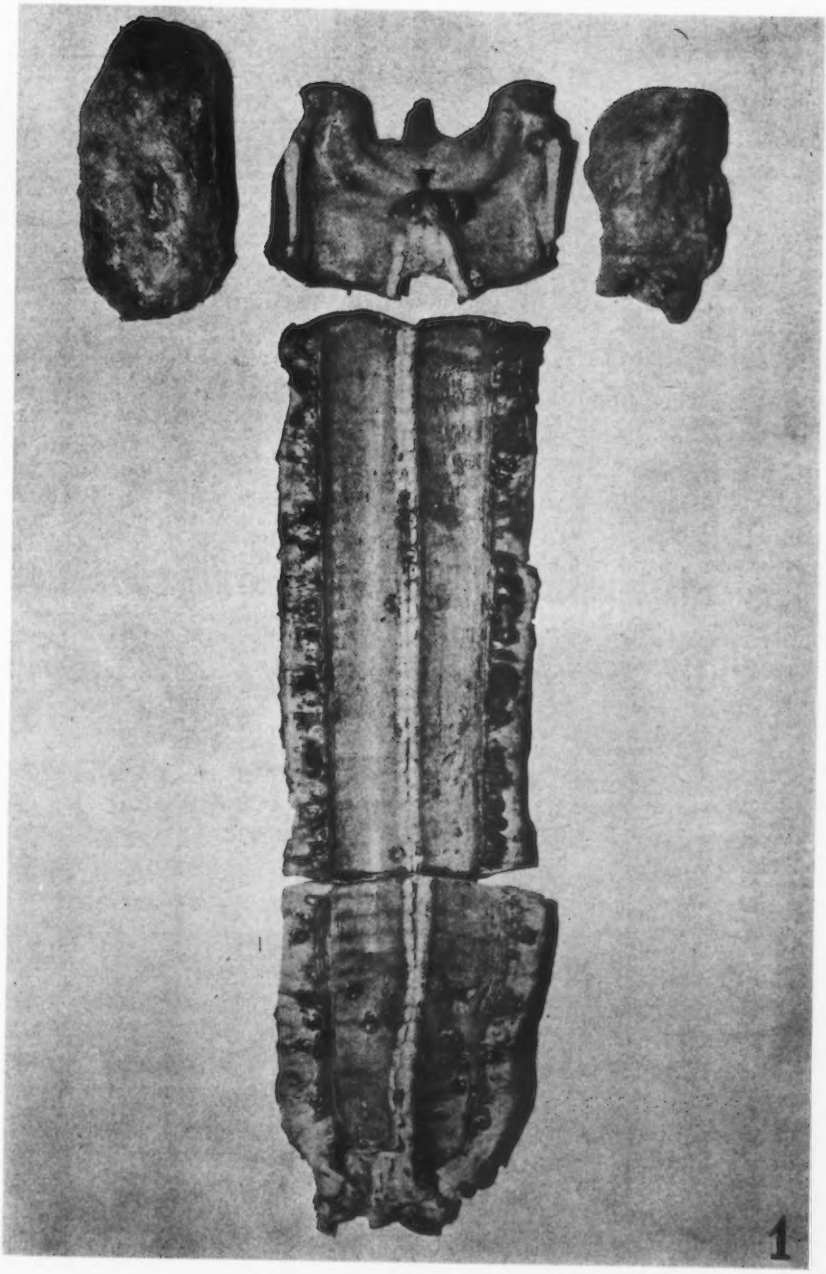
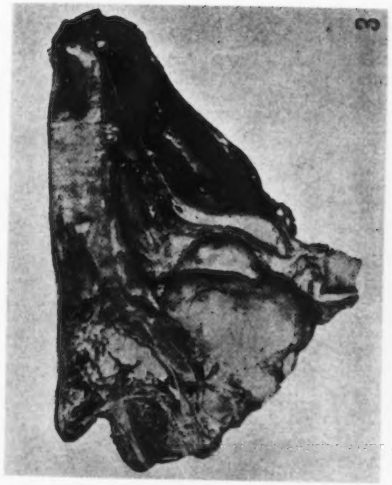
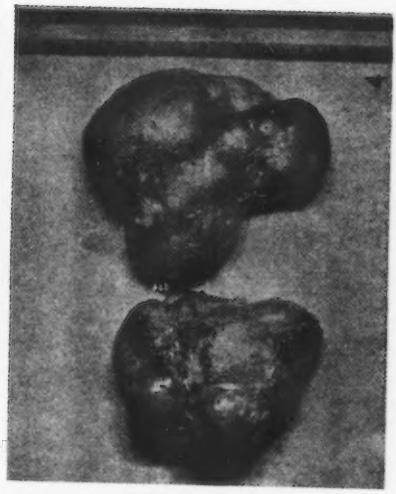


PLATE II





THE REVERIFICATION OF A FOUR-METRE RULE[1]

By R. H. Field[2]

Abstract

An investigation is described in which a determination was made of the length equation of a four-metre invar rule used as a basis for measuring tapes. A short description of the rule and its associated apparatus is given. The investigation demonstrated that different rules made at the same time from the same ingot of invar do not necessarily have identical thermal coefficients. It was also found that the temperatures of two rules of different cross section differed considerably even in a room where the air temperature was changing only at a very slow rate *i.e.*, 1° C. in two or three hours.

Introduction

The base* employed for standardizing measuring tapes in the Division of Physics and Engineering of the National Research Laboratories, Ottawa, consists of a series of concrete piers rising from a monolith beneath the floor and spaced at four-metre intervals. Each pier carries a bracket on which is mounted a horizontal graduated plate or bench mark. Electric radiators under thermostatic control, together with thick insulated walls and the absence of windows, permit a very steady temperature to be maintained throughout the room.

The Four-metre Rule

To measure the intervals between adjacent bench marks an invar rule, four metres in length, is supported on a special carriage which can be moved along a track in front of the piers. This track also serves to support microscope stands and other subsidiary apparatus used in comparing tapes with the base. The four-metre rule and carriage are illustrated in Fig. 1. At the right-hand side can be seen one of the brackets carrying the bench marks.

Naturally it is important that the length of the four-metre rule be accurately known at all temperatures at which tapes are measured, *i.e.*, within the range 0° to 30°C.

Invar, while accepted as the best material for constructing rules of the type under discussion, suffers from the drawback of being subject to secular dimension changes, particularly in the early part of its life. There is doubt also as to whether the thermal equations of nickel steels remain constant during the time that these secular changes occur.

It was originally proposed to send the rule periodically to the International Bureau of Weights and Measures, Sèvres, for verification, but its size is such that there would be an element of risk in this course owing to the adverse

[1] *Manuscript received July 21, 1933.*

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**For a complete description of the tape-verifying base, see Ref. (1).*

effect of shocks that might be received during the journey. Consequently it was decided to acquire one or more one-metre rules and construct apparatus whereby these could be used to measure the four-metre rule as required, metre by metre.

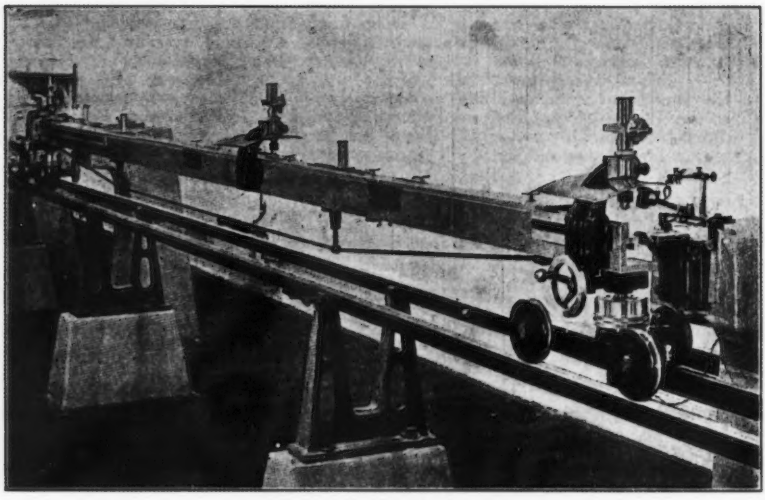

FIG. 1. *Carriage for the four-metre rule employed to measure the tape-standardizing base at the National Research Laboratories, Ottawa. The right end of the rule is just visible near the bench mark bracket.*

The section of the four-metre rule is shown in Fig. 2. The graduations defining its length are ruled to the edge of the exposed neutral surface in order that the rule can be placed opposite the bench marks in such a way that the graduations on rule and bench mark are seen simultaneously in the fields of the observing microscopes. This permits a measurement to be made of the interval between the principal graduations in question.

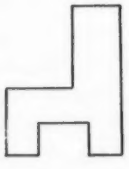

FIG. 2. *Cross section of the four-metre rule (one-half full size).*

Unfortunately the manufacturers found difficulty in machining the rule perfectly straight, and it is appreciably curved in both the horizontal and the vertical planes. The ordinate between the chord joining the edge at the zero and the four-metre graduations and the point of maximum deflection is about 2 mm. An appreciable correction has to be applied, therefore, to reduce the sum of the lengths of the four one-metre chords, as determined by comparison with a one-metre rule, to the length in the direction of the four-metre chord. The magnitude of this correction has been determined by a separate investigation (1, p. 25). Its value is 3.6 μ, and there is no evidence that it varies with temperature by an appreciable amount.

Thermal Equation of the Four-metre Rule

The rule was originally verified by the International Bureau of Weights and Measures in 1913. To determine the thermal dilatation, observations were made by the Bureau on a sample rule, one metre long, made from the same ingot as the four-metre rule. It was assumed that the four-metre rule had the same coefficients as the sample. The thermal equation given in the certificate issued by the Bureau is—

$$\alpha = (1.738\theta - 0.00509\theta^2)\ 10^{-6} \qquad (1)$$

where θ is the temperature on the hydrogen scale.

When the rule was later received in Ottawa an extended series of verifications was made of a number of laboratory standard tapes. It was found in the hot summer weather, when the temperature of the room rose considerably, that all the tapes showed a systematic shortening. As the series ranged from steel tapes expanding about 1 part in 100,000 per degree Centigrade to invar wires with very small but negative thermal coefficients, it was inferred that there was some error in the thermal equation for the rule given by the International Bureau.

At that time (1917-1918) the best method available for checking this equation was to measure the base in winter (when the room temperature can be easily controlled) at three temperatures and compare with the base one or two tapes of which the thermal expansion coefficients had been determined by other laboratories.

Temperatures of 3°, 17° and 26°C. were used in the tests, each temperature being maintained over a period of three days. The base was measured twice each day and the tapes compared with the base six times. This investigation yielded the equation:—

$$\alpha = (1.652\theta + 0.00156\theta^2)\ 10^{-6} \qquad (2)$$

The difference between Equations (1) and (2) was of the correct order to account for the discrepancies previously found at the higher temperatures.

However, the method of obtaining Equation (2) was open to the criticism that the exact thermal coefficients of the tapes used were not known to a degree of precision sufficient to place the results beyond doubt, and means were sought to obtain a more reliable value of it.

Later the proposed apparatus for verifying the four-metre rule by means of one-metre standards was installed. An invar tube about 10 cm. diameter was supported by two concrete piers two metres apart, one pier being that carrying the zero bench mark of the base. The tube bears brackets for holding two micrometer microscopes. Until recently it also carried two hangers, for supporting a steel table fitted with two rollers. These rollers are spaced so that they come beneath the Airy points of the one-metre rule, which is placed on them. A screw on each hanger permits the table and rule to be traversed back, out of the field of view of the microscopes. Alternately a

one-metre chord of the four-metre rule can be brought into the position previously occupied by the one-metre rule, using the adjustments on the four-metre rule carriage.

The steps now in operation for obtaining the length of the four-metre rule are:—

(1) Comparison of a nickel one-metre rule with prototypes of the international metre.

(2) Comparison of this nickel rule with one or more invar rules in the rule comparator, both rules under comparison being immersed in water.

(3) Measurement of the four-metre rule, metre by metre, by comparison with an invar one-metre rule. This operation is conducted in air with the aid of the apparatus briefly described above.

The first one-metre rule, No. 191, of invar, was obtained in 1919. At that date the nickel rule had not been received and there was some doubt as to the exact length and the stability of No. 191. Observations made by the Bureau of Standards at different times gave values for the length of No. 191 differing by as much as 5 μ. It was not until 1928 that this discrepancy was cleared up, by which time the laboratories at both Ottawa and Washington had been equipped with new comparators for verifying standard rules.

Tests made in the one-metre dilatation comparator of this laboratory confirmed the accuracy of the thermal coefficients of rule No. 191. In this case the coefficients had been determined by the International Bureau from direct observations on the rule itself. Further investigations, in course of which rules and observers were exchanged between Ottawa and Washington and the Ottawa standards were compared directly with the legal prototype metre of the United States, gave concordant results and it was felt that the length of the invar rule No. 191 could be relied upon to within 0.1 or 0.2 μ.

Furthermore, a new rule, No. 751 of "Fixinvar" (a new alloy said to be less subject to secular change than invar) was obtained. This rule has a thermal expansion of about one-half that of the four-metre rule or No. 191, *i.e.*, about one part in 10^6 per degree Centigrade. With two invar rules available, of which the length and thermal coefficients were accurately known, it was considered that a redetermination should be made of the equation of the four-metre rule.

Investigations of 1932-1933

Previous measurements of the four-metre rule by means of No. 191 had not given such good agreement among themselves as would be expected from the degree of concordance of the actual observations. Therefore before beginning the measurements means were sought for improving their precision.

Temperature

The comparisons are conducted in air after the rules have been resting side by side for several hours. In view of the steady temperature of the room it had been assumed that both rules had the same temperature, which was taken as that given by two thermometers on the four-metre rule. Some doubt was cast on this assumption by the fact that during an observation, which lasts about 40 min., the temperature so indicated changed by varying amounts up to 0.5°C. As the rules are of different cross-sectional area it is not likely that both would radiate heat at the same rate.

Accordingly provision was made to mount four thermometers on each rule, the bulbs being protected as far as possible against radiation from objects other than the rules. It was found that the temperatures of the two rules did not change at the same rate nor was the difference between their temperatures constant from test to test. The short rule was found always to have a higher mean temperature by an amount varying from 0.15°C. to 0.45°C. owing, presumably, to the necessary presence of the observers. The test program was therefore altered to provide for the thermometers to be read four or five times during the comparison period.

Table I shows the temperatures recorded by the eight thermometers (after correction for scale errors) during a typical comparison. The readings 1, 2, 3, etc., were taken at approximately five-minute intervals. On the four-metre rule a thermometer was placed near the centre of each metre interval and on the one-metre rule the bulbs of thermometers *F* and *H* were about 5 cm. from the ends of the rule, those of *E* and *G* being near the centre. The higher readings of *F* and *H* were undoubtedly due to the proximity of the observers at the microscopes. In calculating the results of the observations the temperature of each rule was taken as the mean of the indications of the group of four thermometers read during the comparison.

TABLE I

TEMPERATURES RECORDED DURING A MEASUREMENT OF THE FOUR-METRE RULE

Reading No.	Temperature, °C.							
	Four-metre rule				One-metre rule			
	A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
1	17.20	17.23	17.21	17.27	17.27	17.57	17.27	17.49
2	.25	.29	.27	.28				
3	.30	.34	.32	.33	.52	.76	.56	.68
4	.31	.36	.35	.36				
5	.33	.39	.37	.39	.68	.85	.75	.83
6	.35	.42	.40	.42				
7	.38	.45	.44	.46	.78	18.03	.85	.92
8	.40	.47	.45	.47				
9					.83	.07	.94	.95
	Mean during observation:—17.36°C.				17.73°C.			

Rigidity of the Apparatus

Observations made with the two rules, Nos. 191 and 751, did not agree as well as was anticipated, and a search was made to ascertain the reason. Improved microscopes were first fitted to the apparatus which was readjusted before each set of observations. Soon it became evident that an error was introduced when the one-metre rule and its supporting table were traversed back so that the edge of the four-metre rule could be brought into the field of view of the microscopes. At the time the apparatus was installed it was thought no appreciable error would be introduced from this cause. The torque produced by the movement of the rule is barely detectable by a sensitive level vial and it was concluded that any component of the movement of the microscope axes at 90° from the direction of rule movement would be negligible. A closer study, however, showed that there was a slight error traceable to this cause. The error (perhaps fortunately as it permitted its discovery) could be changed by an appreciable amount, *i.e.*, enough to change the apparent length of the four-metre rule by several microns, by making almost imperceptible changes in the verticality of the microscopes.

Accordingly the rule-supporting hangers were removed from the invar tube, and the one-metre rule table and the traversing slides were carried from a piece of 2 by 4 in. wooden rod attached to the concrete piers. The invar tube became merely a bridge to carry the microscopes. With this change a considerable improvement was found in the concordance of the final results. Despite readjustments of the apparatus the computed length of the four-metre rule remained within a micron of the mean value, which is of the same order as the errors of observation.

Determination of the Equation of the Four-metre Rule, 1933

Observations were made at three temperatures, and on most days the rules were compared three times. The procedure during a comparison was as follows:—microscopes pointed on: (*a*) one-metre rule; (*b*) interval 0–1; (*c*) interval 1–2; (*d*) one-metre rule; (*e*) interval 2–3; (*f*) interval 3–4; (*g*) one-metre rule; (*h*) interval 3–4; (*i*) interval 2–3; (*j*) one-metre rule; (*k*) interval 1–2; (*l*) interval 0–1; (*m*) one-metre rule.

The temperature of the one-metre rule was recorded between the interchange of observers at *a*, *d*, *g*, *j* and *m*, and that of the four-metre rule was taken between *b* and *c*, *e* and *f*, *h* and *i* and *k* and *l*. A set of observations consumed about 45 min.

The lengths and temperatures of the four-metre rule measured during the tests are given in Tables II and III, which also show the computed lengths of the rule using Equation (5) below, derived as a result of this investigation.

In calculating the equations it was assumed that the expansion of the four-metre rule was linear over the range of temperature covered by each of the three groups of comparisons. The greatest error involved is of the order of 1 μ, and with the exception of one case the errors are much less than this. Hence, with the order of the precision sought, 1 to 2 parts in 4,000,000, the extra labor of a least square reduction was not justified.

TABLE II

MEASUREMENT OF FOUR-METRE RULE IN TERMS OF RULE 191

Date 1933	Four-metre rule		Four-metre rule, computed (Eq.5)	Observed − computed
	Temp., °C.	Length, 4 m.		
Feb. 7	4.72	−6.7 μ	−6.7 μ	0.0μ
	4.87	−5.6	−5.6	0.0
	4.99	−5.0	−4.8	−0.2
Feb. 8	4.72	−6.3	−6.7	+0.4
	4.93	−5.3	−5.2	−0.1
	5.03	−2.9	−4.5	+1.6
Feb. 11	4.63	−7.0	−7.3	+0.3
	4.80	−5.8	−6.1	+0.3
	4.82	−5.9	−6.0	+0.1
Feb. 13	4.76	−6.1	−6.4	+0.3
	4.78	−6.0	−6.2	+0.2
	4.80	−5.5	−6.1	+0.6
Feb. 24	17.35	+78.8	+78.2	+0.6
	17.34	+79.3	+78.1	+1.2
	17.33	+79.4	+78.1	+1.3
Mar. 2	28.69	+151.7	+151.1	+0.6
	29.57	+156.7	+156.7	0.0
	30.22	+160.4	+160.7	−0.3
Mar. 3	29.36	+153.9	+155.4	−1.5
	29.69	+157.3	+157.4	−0.1
	30.11	+159.2	+160.1	−0.9
Mar. 7	30.13	+160.3	+160.2	+0.1
	30.18	+160.5	+160.5	0.0
	30.31	+161.2	+161.3	−0.1
Mar. 8	30.20	+160.6	+160.6	0.0
	30.48	+163.9	+162.4	+1.5
	30.46	+161.8	+162.2	−0.4
April 24	17.73	+83.1	+80.7	+2.4
	17.89	+82.1	+81.7	+0.4
	17.96	+83.7	+82.2	+1.5
April 25	17.05	+75.6	+76.2	−0.6
	17.27	+79.3	+77.7	+1.6
	17.38	+78.9	+78.4	+0.5

TABLE III

MEASUREMENT OF FOUR-METRE RULE IN TERMS OF RULE 751

Date 1933	Four-metre rule		Four-metre rule computed (Eq.5)	Observed − computed
	Temp., °C.	Length, 4 m.		
Jan. 25	18.49	+84.8 μ	+85.7 μ	−0.9 μ
	18.57	+84.6	+86.2	−1.6
	18.67	+84.6	+86.8	−2.2
Feb. 3	4.55	−8.7	−7.8	−0.9
	4.85	−6.7	−5.8	−0.9
	5.05	−5.6	−4.4	−1.2
Feb. 6	4.63	−7.5	−7.3	−0.2
	4.77	−6.4	−6.3	−0.1
	4.90	−5.3	−5.4	+0.1
Feb. 9	4.59	−7.3	−7.5	+0.2
	4.75	−6.1	−6.4	+0.3
	4.85	−5.9	−5.8	−0.1
Feb. 10	4.48	−8.9	−8.3	−0.6
	4.67	−7.2	−7.0	−0.2
	4.78	−5.6	−6.2	+0.6
Feb. 23	17.35	+78.2	+78.2	0.0
	17.37	+77.6	+78.3	−0.7
	17.36	+77.4	+78.2	−0.8
Feb. 28	30.28	+161.7	+161.1	+0.6
	30.60	+164.0	+163.1	+0.9
	30.65	+163.5	+163.4	+0.1
Mar. 1	30.23	+161.7	+160.8	+0.9
	30.55	+163.0	+162.8	+0.2
	30.68	+163.6	+163.6	0.0
Mar. 4	30.27	+160.9	+161.1	−0.2
	30.34	+161.7	+161.5	+0.2
	30.32	+161.2	+161.4	−0.2
Mar. 6	30.18	+160.7	+160.5	+0.2
	30.41	+162.5	+161.9	+0.6
	30.36	+161.5	+161.6	−0.1
April 21	17.75	+79.9	+80.8	−0.9
	17.84	+80.6	+81.4	−0.8
	17.90	+81.5	+81.8	−0.3
April 22	17.74	+80.0	+80.7	−0.7
	17.90	+79.8	+81.8	−2.0
	18.00	+81.3	+82.4	−1.1
	18.06	+82.0	+82.8	−0.8

The equations found for the four-metre rule were:—

From the observations with rule No. 191, alone,

$$L_{191} = 4m + (-39.79 + 7.159\theta - 0.0175\theta^2)10^{-6} \quad (3)$$

From the observations with rule No. 751, alone,

$$L_{751} = 4m + (-38.79 + 6.787\theta - 0.0059\theta^2)10^{-6} \quad (4)$$

The mean of Equations (3) and (4) is—

$$L = 4m + (-39.29 + 6.973\theta - 0.0117\theta^2)10^{-6} \quad (5)$$

The difference between Equations (3) and (4) is—

$$L_{191} - L_{751} = (-1.00 + 0.372\theta - 0.0116\theta^2)10^{-6} \quad (6)$$

Equation (6) has a maximum value at 16.04°C. when its value becomes 1.99 μ, or 1 in 2,000,000 of the length of the rule.

The difference between Equations (1) and (5) is—

$$L_{N.B} - L_{N.R.L} = -0.021\theta - 0.0086\theta^2 \quad (7)$$

Equation (7) gives a value of about 8.1 μ or 1 part in 500,000 at 30°C. This is the order of the shortening found in the laboratory standard tapes verified at this temperature when their lengths were computed from the equation of the four-metre rule given by the International Bureau of Weights and Measures.

The One-metre Rules

Rule No. 191. Invar rule 191 is of an inverted T-section, with graduations ruled to the edge of the exposed neutral surface. One edge is graduated throughout in millimetres from 0 to 1000, with an extra millimetre beyond each end of this range subdivided to 0.1 mm. The thermal expansion determined by the International Bureau of Weights and Measures is

$$\alpha = (2.117\theta - 0.00503\theta^2)10^{-6}$$

Rule No. 191 bears the inscription "Coulée 1209" which is also stamped on the four-metre rule. Hence it would appear that it furnishes further evidence that different samples of invar from the same ingot will not have identical thermal coefficients.

Rule No. 751. Fixinvar rule No. 751 is of orthodox H-section, with graduations, similar to those on No. 191, ruled along the axis on the neutral surface. The thermal equation determined by the International Bureau of Weights and Measures is

$$\alpha = (0.997\theta + 0.00402\theta^2)10^{-6}$$

Thermometers

The temperatures of the rules were measured by Poulenc mercury thermometers subdivided to 0.1°C. Their corrections in the horizontal position were determined by comparison with the standard thermometers of the Division.

Reference

1. Topographical Survey of Canada. Department of the Interior Ottawa. Bull. 44. 1921.

ON THE THERMAL CONDUCTIVITY OF VARIOUS INSULATORS AT ROOM TEMPERATURE[1]

By C. D. Niven[2]

Abstract

The values for thermal conductivity of various common materials chiefly used in the walls of houses are given. By plotting the results obtained, as well as those obtained by other experimenters, on a density-conductivity diagram there is a general indication that at higher densities thermal conductivity increases with increase of density much more rapidly than it does at low densities.

Introduction

The thermal conductivity of many of the commoner materials has become a matter of some economic importance ever since the public have appreciated the fact that by insulating the walls of houses, substantial savings in fuel consumption can be effected. To ascertain the efficiencies of the various thermal insulators a hot plate was erected at the National Research Laboratories at Ottawa about two years ago; the description of this apparatus has already been published in this journal (3) together with an account of an extensive investigation on the thermal conductivity of fibre board. That work was undertaken largely with a view to ascertaining the various factors involved in carrying out accurate measurements on a hot-plate apparatus.

In this communication, the data on other materials are set out and a general comparison is made of various substances. In order to avoid comparisons between the products of the makers and sellers of these materials it has been thought wise to omit the trade names. The scientific value of the results is not in any way impaired thereby. In order not to confuse the reader by the mere use of numbers the materials have been classified to some extent. Boards have been designated by the letter B, soft materials by the letter S, fillers by the letter F, and some miscellaneous materials by the letter M; a single descriptive word usually has been given in brackets. This may serve to remind the reader, when reading the table of values, of the full description of the material given in the text. As the data are of economic interest the words "Canadian" or "imported" have been added, to indicate whether or not the insulator is a Canadian product.

Experimental Data

The units in which the results are expressed are as follows:—Thickness in inches: moisture in %: density in pounds per cubic foot: mean temperature in degrees Fahrenheit: conductivity in B.T.U. per hour, per square foot, per degree Fahrenheit, per inch. The results are presented in Table I. Values

[1] *Manuscript received June 28, 1933.*

Contribution from the Division of Physics, National Research Laboratories, Ottawa, Canada.

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which have been already reported by the writer (3) have not been repeated; reference, however, has been made to them in the text. The descriptions of the materials measured are as follows.

B 1 (*Wood-fibre*)—*Canadian.* This board is made from wood-fibre; four different thicknesses or kinds have been tested, namely one-inch, half-inch, one-inch low density and two-inch. For results see Ref. 3, pp. 123-125. It is there referred to as Wood Fibre No. 1. The results on a two-inch sample, not reported at that time, are given in Table I.

B 2 (*Wood-fibre*)—*Canadian.* This is a board somewhat similar to *B* 1; the fibre is to all appearances slightly larger. Two thicknesses were measured, namely one-inch and half-inch. For results see Ref. 3, pp. 123-125. This board is there referred to as Wood Fibre No. 2.

B 3 (*Bagasse*)—*Imported.* This is a board made from sugar-cane waste. The fibres in it are much longer than those in either of the wood-fibre boards referred to already. For results see Ref. 3, pp. 123-125.

B 4 (*Wood-fibre*)—*Canadian.* This board is somewhat similar in appearance to *B* 2. A half-inch sample was measured.

B 5 (*Laminated*)—*Canadian.* This board consists of five pieces of soft cardboard-like material stuck together with asphalt.

B 6 (*Cardboard*)—*Canadian and Imported.* This looks like a very thick rigid cardboard; it is more of a house lining than an insulator.

The first two results in Table I refer to a different make of board from that to which the last three refer. The boards, however, were so similar that they have all been grouped as *B* 6.

B 7 (*Cork*)—*Imported.* Only one-inch samples were measured.

B 8 (*Plaster Board*)—*Canadian.* This board consists of gypsum plaster between two sheets of paper. It has a perfectly smooth hard finish and is fairly strong but can hardly rank as an insulator as its thermal conductivity is high.

B 9 (*Plaster Board*)—*Imported.* Both samples of this board were much thinner than *B* 8, although otherwise similar in appearance.

S 1 (*Flax Waste*)—*Canadian and Imported.* This material is made from flax waste and comes in sheets about $\frac{3}{4}$ in. thick. It resembles a mat but is not strong and requires to be supported in position.

S 2 (*Eel Grass*)—*Canadian and Imported.* This consists of eel grass packed between two sheets of brown paper and held in place by sewing right through.

S 3—*Imported.* This is a woolly material from wood sewn between sheets of brown paper somewhat like *S* 2.

S 4 (*Animal Wool*)—*Canadian.* This board consists of wool sewn between sheets of paper.

S 5 (*Sheep's Wool*)—*Canadian.* Sheep's wool as used for clothing sewn between two sheets of thick paper; the product is much thicker than *S* 4.

F 1 (*Plaster Board Trimmings*)—*Canadian.* This is a composite mixture of gypsum and paper.

F 2 (*Asbestos Cement*). This is the common asbestos cement powder.

F 3 (*Sawdust*). Ordinary sawdust, and sawdust containing 13.6% calcium chloride.

F 4 (*Fibre Board Trimmings*)—*Canadian.* This consists of trimmings off the fibre board *B* 2.

F 5 (*Gypsum*). This is a gypsum product which, when mixed with water and poured into a mold, sets as a porous mass making a good insulator, provided the manufacturer's instructions are properly carried out. In practice it is found that this is not always the case.

F 6 (*Asbestos and Crushed Rock*)—*Canadian.* Three samples of mixtures of asbestos and crushed rock were tested.

M 1 (*Lime and Diatomite*)—*Canadian.* Three samples consisting of lime and diatomite (percentages not known) were tested.

M 2 (*Aluminium Foil, Spaced*). A sample, consisting of three sheets of aluminium foil and two sheets of paper stretched on a frame about one inch thick, was tested. The three aluminium sheets were inside and the two sheets of paper on the outside. They were spaced to give four equal air spaces.

M 3 (*Paper, Spaced*). A sample somewhat similar to *M* 3, made of four sheets of common blue-print paper stretched on a frame about one inch thick, was tested.

M 4 (*Concrete and Cinder*)—*Canadian.* A thick slab of concrete and cinder was tested. The results are not of great value because the moisture could not be accurately ascertained.

TABLE I

SUMMARY OF RESULTS

Material	Thickness, in.	Moisture, %	Density, lb. per cu. ft.	Mean temp. °F.	Conductivity, B.T.U. per hr., per sq. ft., per °F., per in.
B. 1. (wood-fibre) Canadian	2.128	6.9	19.1	54	0.46
B. 4. (wood-fibre) Canadian	0.520	4.3	16.0	52	0.358
B. 5. (laminated) Canadian	0.471	6.5	20.7	43	0.346
	0.474	6.5	20.6	46	0.340
	0.434	5.9	24.5	45	0.390
	0.433	5.9	24.4	50	0.391
B. 6. (cardboard) Canadian and Imported	0.199	7.8	31.8	54	0.449
	0.198	7.8	31.9	46	0.449
	0.178	6.6	34.8	49	0.481
	0.182	6.6	34.9	48	0.487
	0.182	6.6	34.9	54	0.486

TABLE I

SUMMARY OF RESULTS

Material	Thickness, in.	Moisture, %	Density, lb. per cu. ft.	Mean temp. °F.	Conductivity, B.T.U. per hr., per sq. ft., per °F., per in.
B. 7. (cork)	0.998	1.56	9.6	46	0.280
Imported	1.029	0.9	11.5	46	0.302
	0.996	1.9	11.3	47	0.313
	0.997	1.4	10.6	45	0.297
B. 8. (plaster board)	0.379	8	48.8	31	0.998
Canadian	0.381	5.6	48.4	29	1.06
	0.507	10	52	54	1.15
containing particles of zonolite	0.524	11	54	53	1.23
containing particles of wood	0.497	10.5	49	53	0.99
B. 9. (plaster board)	0.379	—	57.5	36	0.936
Imported	0.235	—	57.9	35	0.726
S. 1. (flax waste)	0.833	6.4	10.8	50	0.323
Canadian and Imported	0.754	6.4	10.8	49	0.334
S. 2. (eel-grass)	0.228	9.7	6.5	46	0.251
Canadian and Imported	0.222	9.0	6.6	46	0.229
S. 3. Imported	0.397	6.6	6.0	55	0.262
	0.403	6.6	5.8	53	0.267
S. 4. (animal wool)	0.273	8.1	7.9	51	0.229
Canadian	0.270	7.5	7.8	49	0.243
S. 5. (sheep's wool)	0.502	6.7	8.7	53	0.244
Canadian	0.400	8.8	6.8	59	0.235
	0.483	7.8	9.2	53	0.242
F. 1. (plaster board trimmings)	1.174	6.3	32	49	0.610
Canadian					
F. 2. (asbestos cement)	1.130	1.0	45	44	1.1
F. 3. (saw dust)	1.202	8	8.7	48	0.373
with 13% $CaCl_2$	1.177	12.4	10.9	45	0.377
F. 4. (fibre-board trimmings)	1.099	5	5.0	43	0.304
Canadian	1.075	5	3.1	44	0.284
	1.092	5	7.3	47	0.298
F. 5. (gypsum)	1.021	0.9	11	46	0.357
F. 6. (asbestos and crushed rock)	1.079	0.5	80	65	1.48
Canadian	1.079	0.6	74	66	1.32
	1.079	0.6	71	64	1.31
M. 1. (lime and diatomite)	1.341	2	42	56	0.87
Canadian	1.281	Less than 1	80	45	1.86
	1.409	1.6	101	48	2.92
M. 2. (aluminium foil, spaced)	1.248	—	—	55	0.253
M. 3. (paper, spaced)	1.095	—	—	45	0.392
M. 4. (concrete and cinder) Canadian	2.690	—	48.5	58	1.28

Comparison of Results

The thermal conductivity of any substance is generally affected by the mean temperature of the sample and by its moisture content; in certain cases, the duration of test may actually affect the results. But on the assumption, that these factors are small in comparing the results, some rather interesting conclusions can be drawn regarding the relation between density and thermal conductivity.

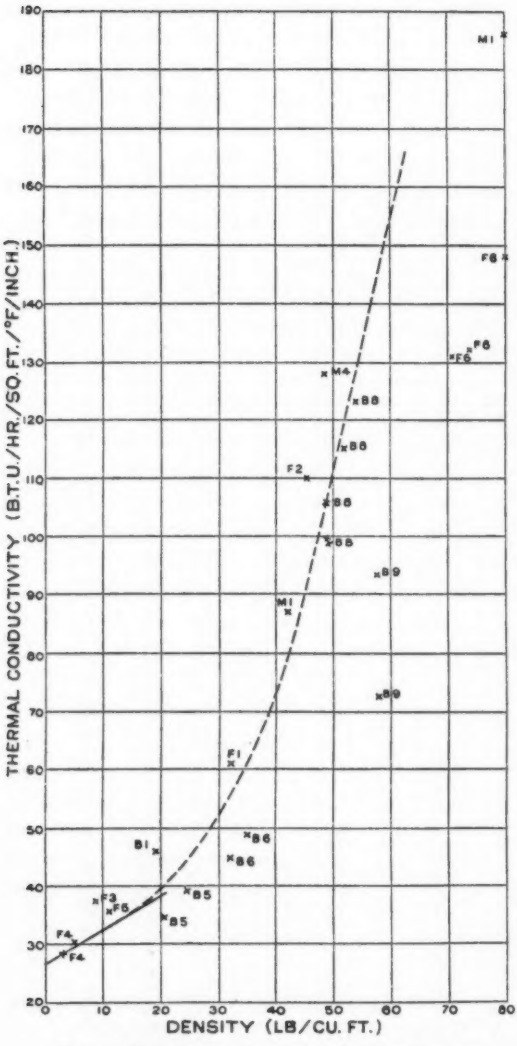

FIG. 1. *Graph showing that when the thermal conductivities of the materials tested are plotted against the densities, the points are grouped roughly about a curve.*

If the conductivities for one-inch and half-inch samples of fibre board be plotted against the densities, it has been shown in the paper previously published that the points lie approximately on a straight line. If the results on a two-inch sample of *B* 1 be plotted on such a diagram, it is found that the point lies considerably off the line; in fact, the conductivity of the two-inch board is very much higher than might be expected from the linear relation. Possibly this is due to the arrangement of the fibres. As mentioned in the previous paper, Finck (2) has proved that when the fibres of a material lie across the direction of heat flow the material has greater heat resistance than when they lie along that direction, and strange to say, this point lies nearly on the extrapolated curve through the points plotted from Finck's results on bagasse in the bone-dry condition. Finck's results, as well as the results obtained by other experimenters on fibre board, have been plotted by the writer and it has been found that they lie around the straight-line

relation connecting density and conductivity for dry material. The diagram has not been reproduced in this paper because it was necessary to apply corrections to some of the actual results of the experimenters in order to make their results apply to a mean temperature of 90°F. and a moisture content of 0%. The diagram, however, pointed to the conclusion that the straight line gives an average value for sheets made from vegetable fibres, and on this assumption one should therefore expect that the results on *S* 1 (flax waste) and *S* 3 should also lie on this line. By actually plotting these results, it becomes clear that *S* 1 does lie near the line but not *S* 3. If the results for *S* 2 (eel grass) be plotted on this diagram the point lies still farther off; this is perhaps to be expected because the fibre is long and flat and lies across the direction of heat flow. The results on *S* 4 (animal wool) and *S* 5 (sheep's wool), when plotted, indicate that animal wool fibres are better insulators than vegetable fibres. The material *B* 5 is laminated and its conductivity is lower than one would expect for a fibre board of similar density. The results on *B* 6 (cardboard) have been plotted on this diagram but as the densities are much higher than those of the fibre boards it is unsafe to draw any conclusions, expecially in view of the results on materials of higher density.

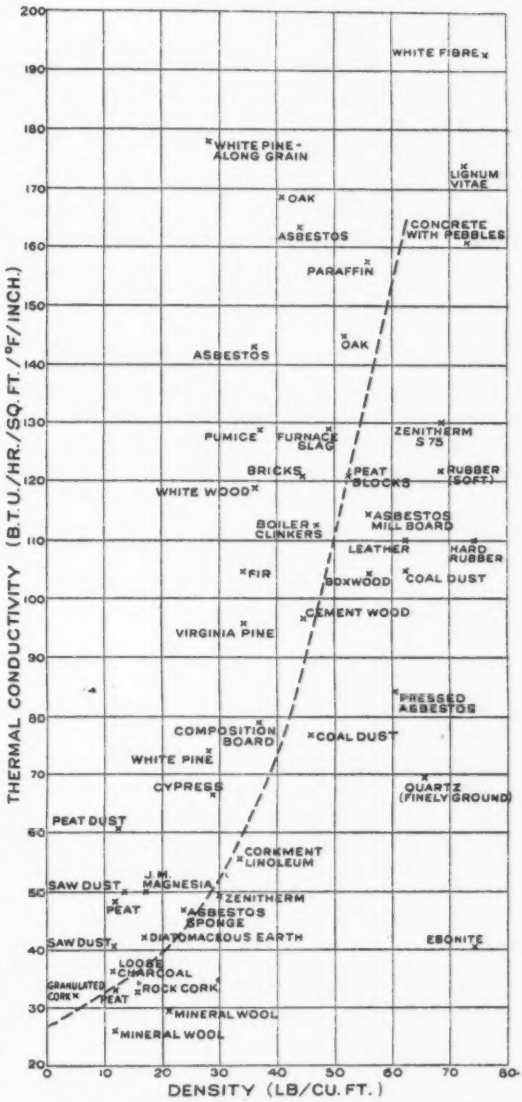

FIG. 2. *Graph showing results taken from A.S.R.E. circular (1) in relation to curve in Fig. 1.*

It has been found that when the results on materials of higher density are plotted, the points thus obtained lie very roughly on a curve. The points are plotted on Fig. 1. In Fig. 2 this curve, on which the points roughly lie, is reproduced and the results on a number of substances are plotted; these results have been taken from the tables at the end of a report by the A.S.R.E. insulation committee (1).

The line near the origin on Fig. 1 is the line obtained for fibre boards. It becomes now very obvious that although *B* 6 does lie on this straight line when produced, we have no right to conclude that a straight-line relation holds between density and conductivity for vegetable fibres with a density greater than 20.

It is not the purpose of this paper to discuss the results plotted in Fig. 2; that diagram serves, however, to confirm the conclusion which may be drawn from Fig. 1, namely, that in general, at higher densities increase in density causes a much greater increase in thermal conductivity than it does at lower densities.

References

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THE SORPTION OF WATER BY ASBESTOS FIBRE[1]

By L. M. Pidgeon[2] and A. Van Winsen[3]

Abstract

The sorption of water by asbestos fibre has been examined using two modifications of the static method. In the first method the sample was weighed in the absence of air by a quartz spring balance, after which the required vapor pressure of water was admitted. In the second method the samples were weighed in air in a room the temperature and humidity of which were controlled. The two methods have given identical results, producing the sigmoid isotherm similar to those found in the cases of cotton and wood, and exhibiting a marked inflexion in the region of the saturation point. The rate of sorption has been examined using the sorption balance and it has been shown that at humidities below 70% equilibrium is established in a few minutes; at higher humidities longer time is required. Because of this and other reasons it is suggested that in this region capillary condensation is taking place.

Introduction

It would appear that the sorption of water should be an important factor influencing the physical properties of a fibrous material like asbestos, which retains its special nature due to the water of hydration. Research carried out in these laboratories on the standardization of asbestos testing has shown this to be the case, as the relative humidity appears to exert a definite effect on the screen-test results. This variation in the screen test must be dependent on the amount of sorbed water which in turn is controlled by relative humidity. The obvious starting point in an examination of this factor is a determination of the amount of sorption under different conditions of humidity.

Very few references to quantitative work of sorption by asbestos are available and in most cases the type of fibre and its previous history are not mentioned. Wilson and Fuwa (4) gave a few values for asbestos in a survey of the moisture relations of a large number of substances, but no details of the fibre are given. It seemed desirable to obtain data on the moisture equilibria of the fibre as it is used in the Quebec standard testing machine. This paper describes experiments carried out by two different methods to find the amount of sorption over a complete range of humidities from 0 to 96%.

Samples

The samples which were examined were from a standard, milled product of the chrysotile variety, obtained in the province of Quebec. No washing or other treatment was given. The screen test of the fibre was approximately 4–8–4 Quebec Standard Test.

[1] *Manuscript received June 2, 1933.*
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Experimental

The sorption of water was examined by two methods which differ in the procedure by which the required vapor pressure of water was obtained.

Method 1.

A sorption balance was employed, sorption taking place in the absence of air. The apparatus (Fig. 1) was a modification of the arrangement described by McBain and Bakr (2), which has been employed by one of the authors elsewhere (3). The sample was suspended by a fine aluminium wire from a quartz spiral in the chamber *C*. The water was contained in the tube *B* and was freed from dissolved gases in the ordinary manner. The pressure in the apparatus was measured on the manometer *A*, which was filled with an oil of negligible vapor pressure, giving a deflection 15 times that of mercury. The system was evacuated with a two-stage steel mercury diffusion pump backed by an oil pump, with which combination the pressure could be reduced to less than 10^{-5} mm. Hg. The tube containing the quartz spiral was immersed in a thermostat filled with water which was maintained at 20° C. ± .01°.

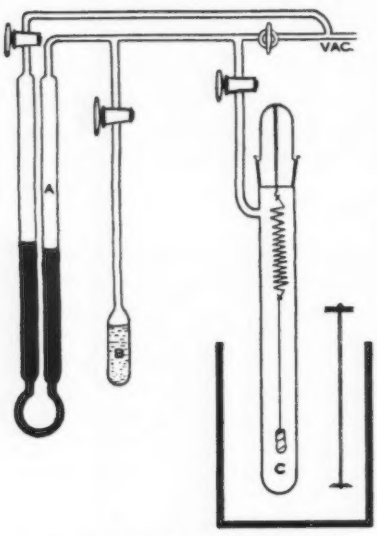

FIG. 1. *Sorption balance.*

A deflection of 1 mm. was produced by a weight of 0.0075 gm., with the cathetometer reading to 0.02 mm.; a change of weight equal to 0.0002 gm. could therefore be detected. Hence with a sample weighing 0.3 gm. the measurements of weight were correct to 0.1%.

Procedure

Two methods of operation are available with this apparatus; they may be called the constant vapor pressure method and the variable vapor pressure method. In the first, the vapor pressure of the apparatus is maintained at a constant value by controlling the temperature of the bulb *B*. This method requires a second thermostat to attain this end. The great advantage is that the sorption takes place at a constant vapor pressure throughout the whole period. In the second method, a certain amount of water vapor is added to the apparatus by momentarily opening the tap over tube *B*. As adsorption takes place the pressure falls until equilibrium is established. This method, while it is much more convenient than the first, is unsuitable if hysteresis effects are to be examined, as adsorption takes place during a falling

vapor pressure, hence some desorption takes place simultaneously. In the present case it was found that the value at any humidity was independent of the direction in which the equilibrium was reached, hence the second method was generally adopted for its convenience.

Method 2

In the second series of experiments the samples were exposed to air of known humidity and temperature in a conditioning room. The temperature was controlled to 0.5° C. by means of a bimetallic thermoregulator. The air in the room was circulated with a fan. The relative humidity was maintained by a mechanical sprayer controlled by a membrane-type humidostat. The humidity was maintained to within 2% of any stated value up to 60% relative humidity, while above this value the variations became more noticeable. The humidostat was periodically checked against an aspiration psychrometer.

Samples (500 gm.) were exposed in this room in such a way as to be protected from any mist or spray. This weight was chosen to satisfy the requirements of the Quebec standard testing machine which requires one-pound samples. Forty eight hours was allowed for the establishment of equilibrium after which the samples were weighed to 0.1 gm. giving an accuracy of weight determination of 0.02%.

In comparing the two methods it may be stated that while the weight determination is much more accurate in the case of Method 2, owing to the large size of the samples which may be employed, the determination of relative humidity is liable to be seriously in error at high values. In the first method the humidity determinations are dependent only on the measurement of temperature and pressure, both of which may be accurately determined. The results in the case of the sorption balance are considered to be more accurate in the region of high humidities, while at lower humidities agreement is almost perfect as will be seen later.

The sorption balance offers additional advantages in that the conditions may be accurately controlled and a wider range of humidities produced, while the time required for the establishment of equilibrium is enormously reduced by the removal of air. The second method is important, however, as it is identical with the conditions which are encountered in practice.

Experimental Results

Definition of "Dry Weight"

It is necessary to define the "dry" weight of all hydrated compounds, as by heating to elevated temperatures it is always possible to drive off more water and the values at any humidity will obviously depend on the dryness which has been chosen as the zero value. It is undesirable to heat asbestos to high temperatures because of the danger of removing part of the water of hydration; hence in the experiments to be described the following procedure was adopted.

In the vacuum method as described above the dry point was obtained by strongly evacuating the sample at 20°C. A constant reproducible weight was reached after a few hours, evacuation upon which the subsequent calculations were based. For Method 2 the dry point was obtained by heating the sample in air at 105°C. for 16 hr. The data to be given show that these methods give identical results. It follows, therefore, that heating to 105°C. has no effect on the chemically bound water or on the power of adsorption.

TABLE I

SORPTION OF WATER BY ASBESTOS FIBRE

Method 1 Temperature 20°C.		Method 2 Temperature 25.5°C.	
Relative humidity, %	Sorption, %	Relative humidity, %	Sorption, %
6.5	0.5	24	0.82
11.3	0.7	33	0.97
27.6	0.9	40	1.09
49.5	1.2	50	1.16
63.0	1.4	60	1.32
68.0	1.5	70	1.57
78.7	1.9	80	2.10
85.6	2.2	90	2.53
96.6	3.3	96	3.14

The results shown in Table I are plotted in Fig. 2 and show good agreement between the two methods except at high humidities. It may be safely assumed that the results by Method 1 will be more nearly correct above 75% relative humidity. The curve is of the familiar sigmoid shape which characterizes many sorption processes. Three definite regions are in evidence; at low humidities (up to 5%) adsorption takes place at very low pressure causing the curve to rise sharply; then follows a wide region from 20 to 65% in which the isotherm approaches a straight line of definite slope; near the saturation point it again rises sharply giving a relatively high and rather indefinite value for the saturation point. Values as high as 6% have been obtained by allowing the fibre to remain in a saturated atmosphere for some time. The significance of the isotherm will be discussed later.

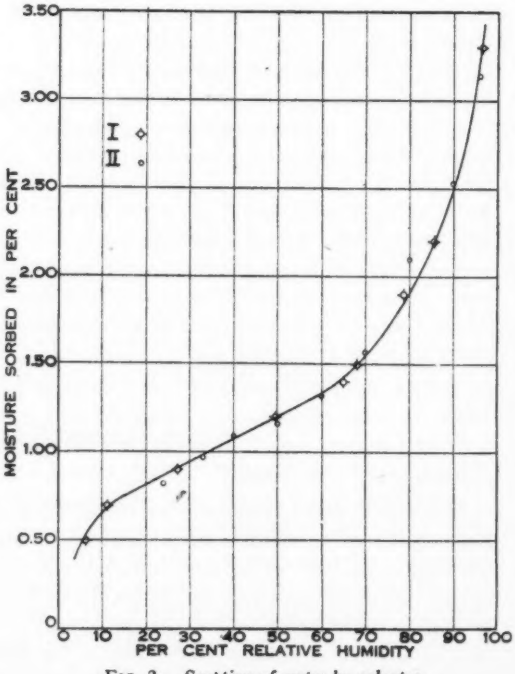

FIG. 2. *Sorption of water by asbestos.*

Rate of Adsorption

The sorption balance offers a convenient method of determining the rate

at which adsorption takes place in the absence of air. Under these circumstances the true rate of adsorption is more closely approached as the molecules of adsorbate are not required to diffuse through inert molecules to reach the adsorbing surface. Any adsorption establishes a pressure gradient which is quickly removed by mass flow of the gas. The procedure which was followed included the evacuation of the sample in the usual manner, after which the tube *B* was placed in communication with the apparatus, the temperature of the water in *B* being controlled to produce the desired vapor pressure. Readings of deflection were taken against time. There was some delay in the establishment of the final vapor pressure owing to the cooling of the water surface by evaporation. This did not appear to be a serious objection as the experiments on rate are largely comparative.

The results of experiments performed at different humidities are plotted in Fig. 3. It is at once apparent that at humidities corresponding to the straight part of the isotherm the equilibrium is established in a few minutes, suggesting a true surface adsorption in the ordinary sense of the term. This rapid adsorption process holds over the straight part of the isotherm, while at high humidities, where the amounts taken up are large, a further process appears to be superimposed. Much longer times are required, the equilibrium being incomplete after the lapse of several hours. The theoretical significance of this will be mentioned below.

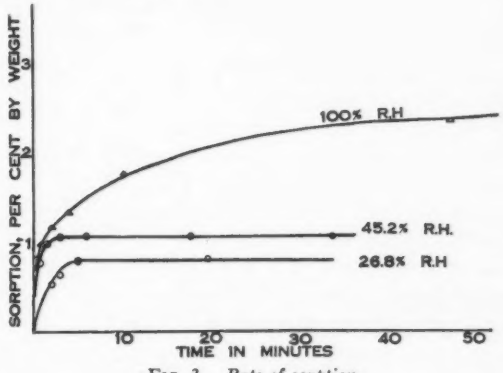

FIG. 3. *Rate of sorption.*

Hysteresis

In the cases of silica gel, aluminium hydroxide, ferric oxide, and other porous inorganic substances, considerable controversy has arisen as to whether the same sorption value at a given humidity may be reached either by gain of water from a less saturated condition or by loss from a higher saturation. This point has been examined for asbestos using the sorption balance. The apparatus was altered by the addition of a one-litre flask containing a sulphuric acid solution, the concentration of which was adjusted to give the desired humidity. A very constant source of relative humidity was obtained by immersing the flask, equipped with a magnetic stirrer, in the thermostat.

At relative humidities of 30.0, 45.0 and 79.0% the same sorption value was reached by adsorption or desorption; hence no hysteresis exists in the case of asbestos fibre over this range. The experimental significance of this fact has been already mentioned.

Discussion

The sorption isotherms for water on asbestos suggest a direct adsorption process which is rapidly completed up to humidities of 70% of saturation. Above 70% the sorption process takes on a new form; not only is the amount of sorption much greater but the time taken to reach equilibrim is a great deal longer. If the results are plotted logarithmically according to the classical sorption isotherm

$$x/m = kp^{1/n}$$

where x/m is the amount of sorption, k and n are constants, and p the pressure, a straight line is obtained for values extending from 5 to 65% of saturation; as shown in Fig. 4. Above the latter value the curve bends sharply toward the sorption axis again suggesting some change in the mechanism of sorption.

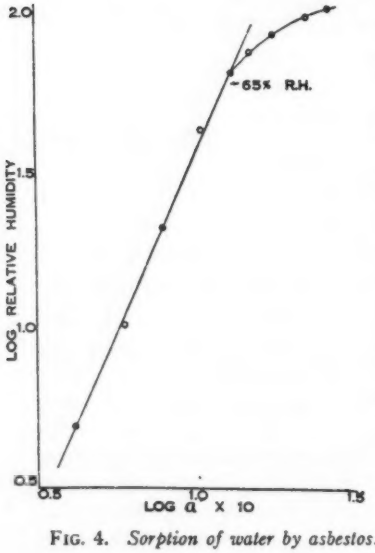

FIG. 4. *Sorption of water by asbestos.*

It is suggested that this upper region is due to condensation of liquid in capillaries. While the evidence for capillary condensation as a general explanation for sorption may not be completely convincing it is generally admitted that in certain instances, where the isotherm is of the shape found here, capillary condensation takes place at high humidities. It is mentioned by McBain (1) that various hydrated oxides (copper, manganese, etc.) show an isotherm which gives evidence of capillary condensation near the saturation point; hence it appears that asbestos may be added to their number.

As mentioned previously the practical importance of this subject lies in its application to standardization of asbestos testing. It is of particular interest, therefore, to have found that the sorption isotherm between relative humidities of 25 and 65% approaches a straight line. If a direct relation may be found between the amount of sorbed water and the physical condition of the fibre as shown by the screen test, the test result at any other humidity should be predictable from one determination together with consideration of the sorption isotherm.

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THE ACTION OF SULPHURIC ACID ON CERTAIN DERIVATIVES OF CYCLOPROPANE[1]

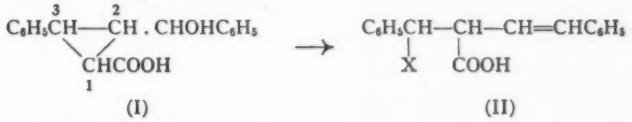
By Charles F. H. Allen[2] and Raymond Boyer[3]

Abstract

A considerable variety of ketocyclopropanes has been submitted to the action of sulphuric acid, alone or in acetic acid. In general, the mode of reaction was similar to, though less drastic than, that of hydrogen bromide; this indicated a similar mechanism. When the cyclopropane ring was attacked, the product isolated was apparently formed by the addition of a molecule of water or acetic acid, or was the result of a secondary reaction dependent on a primary product so formed. The nitriles were hydrolyzed to amides without opening of the ring. A mechanism is suggested to account for the ring scission of cyclopropyl alcohols, which takes place in a different manner from most cyclopropane derivatives.

Kohler and his students have studied in great detail a large number of highly substituted cyclopropane ketones and determined characteristic reactions of each type. The similarity to α, β-unsaturated ketones has been pointed out; in addition reactions involving substances of the type HX, the X was always attached to a β-carbon, just as in 1,4-addition to a conjugated system. As far as addition was concerned the cyclopropane ring was equivalent to an ethylenic linkage (17). This same conclusion has been reached by other investigators; *e.g.*, from a study of absorption spectra Carr and Burt (9) concluded that the cyclopropane ring is very similar in character to an ethylenic linkage and can, therefore, form a conjugated system with a carbonyl group.

The only discrepancy appears in some work of Stoermer (23) in which the action of sulphuric acid, alone or in acetic acid, on the hydroxyacid (I) was shown to give an open chain substance of the type of (II); this could have been formed only by opening of the ring in the 2 : 3-position.



(I) (II)

The purpose of this investigation was to see whether sulphuric acid acted in a different manner from other ring-splitting reagents.

Sulphuric acid was found to be less reactive than hydrogen bromide as would be expected, but the mode of reaction was in general the same. When the cyclopropane ring was attacked the product isolated was apparently formed by the addition of a molecule of water or acetic acid, or was the result of a secondary reaction dependent on a primary product so formed. The reagent was an acetic acid solution of sulphuric acid, the concentration

[1] *Manuscript received May 15, 1933.*
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being varied according to the ease with which the substance reacted*. If the starting material was recovered unchanged, cold concentrated sulphuric acid alone was used. The results are shown in Table I. The positions are numbered in the usual manner (cf. formula I).

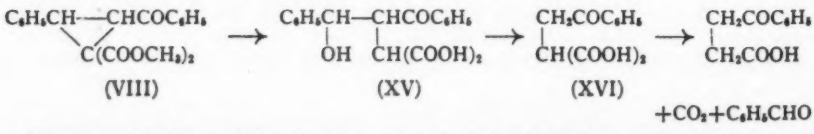
TABLE I

ACTION OF SULPHURIC ACID ON CYCLOPROPANES

No.	Substituents in position			Result	Ring opening	
	1	2	3		by H_2SO_4	by HBr
III	2 H	C_6H_5CO H	2 H	γ-Acetoxybutyrophenone	1,2 or 2,3	1,2 or 2,3 (22)
IV	C_6H_5 C_6H_5CO	C_6H_5CO H	2 H	Unattacked (1)	No	1,2 (1)
V	C_6H_5CO H	C_6H_5CO H	C_6H_5 H	Bimolecular product	Undetermined	1,3 or 2,3 (18) Monomolecular
VI	2 COOR or 2 COOH	C_6H_5CO H	2 H	Unattacked (3)	No	1,2 (3)
VII	COOH H	C_6H_5CO H	2 H	Unattacked (3)	No	—
VIII	2 $COOCH_3$	C_6H_5CO H	C_6H_5 H	C_6H_5CHO $C_6H_5COCH_2CH_2COOH$	1,3 2,3 not excluded	1,3 and 2,3
IX	C_6H_5 $COOCH_3$	C_6H_5CO H	C_6H_5 H	Unattacked	No	1,2†
X	H NO_2	p-ClC_6H_4CO H	C_6H_5 H	Furane (XV)	2,3	2,3 (19)
XI	C_6H_5 NO_2	C_6H_5CO H	2 H	Unattacked until concd., then oils	Undetermined	No
XII	2 H	CN COOR	2 H	Amide ester (XIX)	No	—
XIII	C_6H_5 CN	C_6H_5CO H	C_6H_5 H	Amide (XXIII)	No	No
XIV	2 H	H $(C_6H_5)_2COH$	2 H	Oils	Undetermined	—

† *Unpublished results.*

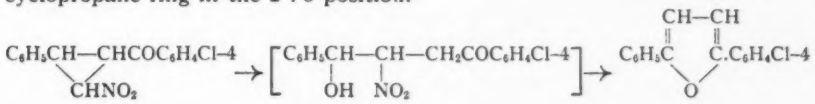
The ester (VIII) gave as final products benzaldehyde and β-benzoyl propionic acid. Two intermediates of known structure (XV, XVI) were isolated, so that the probable course of the reaction is as follows:



Bertram and Walbaum (4) used such a mixture for the hydration of camphene, and it has been applied similarly to other terpenes.

The ring has apparently been opened in the 1 : 3 position; however, the amount of acid (XV) was not sufficient to exclude 2 : 3 ring opening, which would also yield benzaldehyde and acid (XVI).

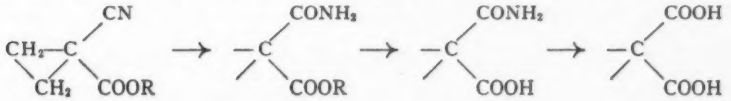
The nitroketone (X) was very easily attacked and gave 2-phenyl-5 (*p*-chlorophenyl) furane (XVII), resembling the behavior of the same substance with hydrogen bromide (1); it was impossible to isolate an intermediate product, but by analogy with the known reaction it should be a hydroxy compound (XVIII). At any rate, the net result has been a splitting of the cyclopropane ring in the 2 : 3 position.



(X) (XVIII) (XVII)

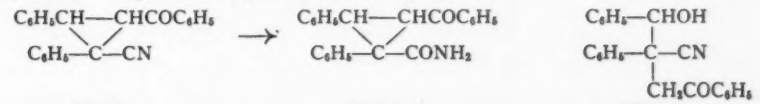
Diels has shown that furane and its methylated homologues react in the diene synthesis, forming addition products with maleic anhydride (11). This addition is apparently blocked by the presence of phenyl groups on the α-carbon, for the furane (XVII), 2,5-diphenylfurane and 2,3,5-triphenyl-4-bromofurane were recovered unchanged after refluxing with maleic anhydride.

The cyclopropane nitriles all reacted alike, being hydrolyzed to amides without ring opening. The nitrile ester (XII) gave the amide (XIX) which was then hydrolyzed to the known dibasic acid (XXI) by alkali, thus showing the ring was still intact. The intermediate acid-amide (XX) was isolated.



(XII) (XIX) (XX) (XXI)

All three stereoisomeric forms of the cyanoketone (XIII) (16) gave the same substance, analyzing for the addition of water and different from the two known open chain stereoisomers (XXII) (16). The new substance is the amide (XXIII); it could not be hydrolyzed by any method tried. On dehydration it gave the cyclic nitrile, m.p. 166° C.



(XIII) (XXIII) (XXII)

A very small amount of a stereoisomeric amide was formed from one of the cyanoketones, as well as being the sole product of the action of ammonia on the ester (IX). It was converted into its isomer by the action of alcoholic hydrochloric acid; the reverse transformation was brought about by acetic anhydride. Cyclopropyl cyanide and 1-phenyl-1-cyanocyclopropane have already been hydrolyzed to amides without opening of the ring by the action of alkali or phosphoric acid (7, 14) and were not included in this work.

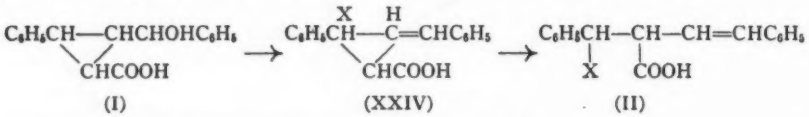
From these results it is evident that there is nothing peculiar about sulphuric acid as a ring-opening reagent; therefore to account for the results described by Stoermer with the hydroxycyclopropane (I) some other mechanism must be devised, especially as hydrogen chloride acted in the same manner to give a chloride (formula II; X-Cl). The following generalizations are suggested:

1. When cyclopropane alcohols in which the OH is on the carbon next the ring are treated with acidic reagents that open the ring, the first step is a dehydration to form a substance having a double bond directly connected to the ring.

2. The system thus formed acts as the equivalent of an allenic linkage and, in addition reactions, adds reagents of the type HX like a highly substituted allene, the X going to an end carbon and the H to the central carbon, with splitting of the ring.

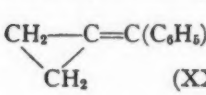
3. When both an alcoholic and carboxyl group are attached to the ring, the former system is more active.

These may be illustrated with substance (I). Stoermer (23) suggested that (XXIV) might be an intermediate product in the reaction, though no com-



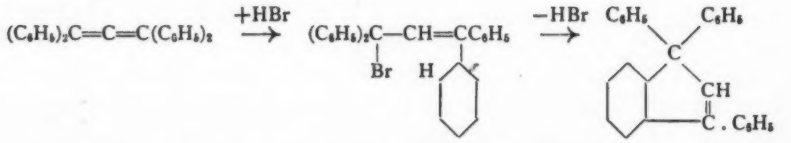
(I) (XXIV) (II)

pound with such a linkage was then known. In a recent attempt to make cyclopropanone, Lipp (20) converted diphenylcyclopropylcarbinol (XIV) to the bromide and removed hydrogen bromide to get (XXV) showing that a substance of this type is capable of existence.



(XXV)

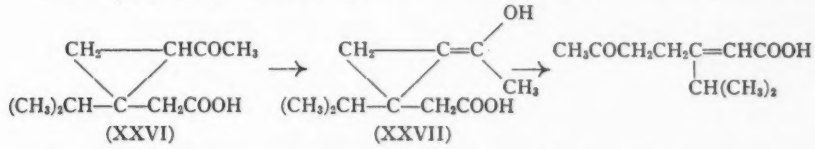
Dimethylallene adds hydrogen bromide to form a saturated dibromide ($(CH_3)_2CBr.CH_2CH_2Br$) (12); whatever the mechanism the bromine atoms go to the ends of the system. When triphenyl allene is treated with hydrogen bromide it isomerizes to triphenylindene (15, 25); this may be represented as addition one way and subsequent elimination of a hydrogen from one of the benzene nuclei:



Similarly, methyl triphenylallene gives methyldiphenylindene (27).

After this mechanism was devised the literature was searched for all substances containing a cyclopropane ring with a hydroxyl group in the required position, and about a dozen compounds were found among the terpenes. In

every case the products actually formed by the action of sulphuric acid agreed with the predictions required by the above. Wallach (26) has suggested that an intermediate enol (XXVII) was formed to account for the unexpected ease of ring opening with the cyclic keto acid (XXVI). However, as this



substance is a cyclopropane ketone, it belongs to the class of substances the reactions of which are considered in the first paragraph, and this assumption is unnecessary.

Experimental

A. Preparation of the Cyclopropane Derivatives

Most of these were made using directions in the literature, but in some instances a variation of the procedure resulted in a better yield.

Benzoylcyclopropane (III). γ-Chlorobutyrophenone was prepared in a 50% yield following Conant's directions (10). Bruylants (6) predicted that the residual solutions should contain most of the other 50% as benzoylcyclopropane, so these were investigated as follows: the solution containing the ketimine was extracted with ether and the extracts from several runs allowed to accumulate until three litres had been obtained. The solvent was then distilled and the residue distilled with steam until diphenyl began to solidify in the condenser; the remainder of the diphenyl was collected separately but not quantitatively—benzoylcyclopropane is not volatile with steam. The oily layer in the first distillate was separated and carefully fractionated with the following results: 1.5 cc. of colorless liquid, b.p. 46° C., probably propyl chloride; 10 gm. of a colorless liquid, b.p. 78° C., D^{22}_4., 0.8505, 0.8508 (*n*-butyl chloride has b.p. 77.9° C., D^{0}_{4} C., 0.907, and D^{14}_{4}, 0.897 (21)); 20 gm. bromobenzene; 3 gm. diphenyl. The residual oil solidified and gave a small amount of a pale yellow solid, m.p. 177° C., which was not investigated. There was no indication of benzoylcyclopropane.

The cyclic ketone was prepared in a 93% yield by substituting potassium cyanide for the hydroxide; 10 gm. of γ-chlorobutyrophenone was added to 4 gm. of potassium cyanide in 100 cc. of absolute methyl alcohol and, since hydrogen cyanide was given off, was left in the hood for 10 days. The potassium chloride was filtered and the solvent allowed to evaporate, leaving the ketone which was then distilled *in vacuo;* 7 gm., b.p. 110–5° C. at 7 mm.; 248° C. at 760 mm. Absolute ethyl alcohol could be used, but the presence of water diminished the yield considerably. Cuprous cyanide acted in a similar manner, but the yield was only 60%; the residues did not give any γ-benzoylbutyric acid on hydrolysis, indicating no substitution of CN for Cl. Again, hydrogen cyanide was given off.

The oxime and semicarbazone were prepared and their melting points agreed with those already recorded. A 2,4-dinitrophenylhydrazone was made in the usual manner; it separated from benzene in fine red needles, m.p. 151° C. Analysis:—Calcd. for $C_{16}H_{14}O_4N_4$: N, 17.2%. Found: N, 16.9, 17.0%.

Methyl 1,3-diphenyl-2-benzoylcyclopropane-1-carboxylate (IX) was prepared in connection with another investigation and will be described in a later paper. Ethyl 1-cyanocyclopropane-1-carboxylate (XII) was secured in a yield of 76% following the procedure of Jones and Scott (13), but using equivalent quantities of halide and ester; ethylene dichloride and chlorobromide could not be substituted for the dibromide without greatly diminishing the yield.

Diphenylcyclopropyl carbinol (XIV). Lipp (20) omitted the yield of this substance in his paper; the present authors did not succeed in obtaining more than 5% of the theoretical amount.

B. Treatment with Sulphuric Acid

(a) Benzoylcyclopropane (III). Sulphuric acid (2 cc.) was added to a solution of 5 gm. of the cyclic ketone in 40 cc. of glacial acetic acid and the mixture boiled for 5 min. The hot, brown solution was poured into water, extracted with ether and the extract washed with dilute sodium carbonate; 4 gm. of γ-acetoxybutyrophenone was obtained which after distillation had a boiling point of 195–200° C. at 40 mm. Analysis:—Calcd. for $C_{13}H_{14}O_3$: C, 69.9; H, 6.8; CH_3COO, 28.6%. Found: C, 69.4, 69.4; H, 6.3, 6.2; CH_3COO, 29.0%.

A mixture of 2.5 gm. of the acetate, 3.5 gm. of phenylhydrazine, 10 cc. of water and 30 cc. of alcohol was allowed to stand overnight. The 1,3-diphenyldihydropyridazine crystallized, and after purification had a melting point of 141° C.; a mixed melting point with a specimen prepared as directed by Conant (10) was not depressed.

The 2,4-dinitrophenylhydrazone, prepared in the usual manner, crystallized in thick red rods from benzene, m.p. 165° C. Analysis:—Calcd. for $C_{18}H_{18}O_6N_4$: N, 14.5%. Found: N, 14.8%.

(b) Methyl 3-phenyl-2-benzoylcyclopropane 1, 1-dicarboxylate (VIII). A solution of 10 cc. of concentrated sulphuric acid, 5 gm. of the ester, and 25 cc. of acetic acid was refluxed for two hours, poured into water, and the mixture extracted with ether. The ether extract was washed first with dilute sodium carbonate solution, then dilute sodium hydroxide. On acidification of the carbonate solution a small amount of an acid, m.p. 118° C., was obtained; this substance was very unstable and could not be recrystallized because of the ease with which it decomposed into benzaldehyde and a solid acid, perhaps because of a trace of base present. A sample was refluxed with alkali for an hour and then distilled with steam; the benzaldehyde in the distillate was recognized by formation of the phenylhydrazone. The residue in the flask was acidified, and after a short time, an acid, m.p. 164–165° C., separated; phenacyl malonic acid (XVI) has a recorded melting point of 178° C. with

decomposition. Accordingly a specimen was prepared as directed in the literature (5), and carefully purified; it melted at 164–165° C., and a mixed melting point was also 164–165° C. On titration with standard alkali neutralization equivalents of 107.5 and 109 were obtained; the calculated value for $C_{11}H_{10}O_5$ is 111.

A sample was heated at 180° C. as long as gas was given off, the residual oil dissolved in sodium carbonate, filtered and acidified. β-Benzoylpropionic acid was deposited and identified by comparison with a sample at hand; by dissolving 2 gm. of the cyclic ester in 20 cc. of concentrated sulphuric acid, pouring upon ice, extracting the oil with ether and hydrolyzing as above, the malonic acid was obtained in one step. A run of this size was carried out quantitatively and 1.2 gm. of acid (86% of the theoretical) found on titration with 0.5 *N* sodium hydroxide.

(c) Methyl 1,3-diphenyl-2-benzoylcyclopropane-1-carboxylate (IX). This ester was recovered unchanged from solution in sulphuric acid, either alone or in acetic acid.

(d) 1,2-Dibenzoyl-3-phenylcyclopropane (V). Two stereoisomeric forms were used and both acted in the same manner. The conditions under which they were treated with the acid were varied considerably, but it was impossible to repeat any given procedure; often the cyclic compound was recovered unchanged. The details that gave the best results follow:—one cc. of sulphuric acid was added to 0.2 gm. of the cyclic compound in 10 cc. of acetic acid (for the isomer melting at 116° C.) and the mixture boiled for 5 min. It was then poured into water, extracted with ether and washed with sodium carbonate solution; a light yellowish amorphous solid remained after the ether was evaporated; it was purified by dissolving in chloroform and precipitated by pouring into methyl alcohol; m.p. 205° C. Analysis:—Found: C, 88.1; H, 5.3%; mol. wt., 586. The isomeric ketone (151°) required 25 cc. of acetic acid to dissolve it but the result was the same.

(e) 1-Phenyl-1-nitro-2-benzoylcyclopropane (XI). The isomer (m.p. 131° C.) was not affected when 1 gm. in 35 cc. of acetic acid containing 5 cc. of sulphuric acid was left overnight, or boiled for 1.5 hr. The mixture (m.p. 80° C.) was wholly converted into the form, m.p. 131° C. More concentrated solutions gave off oxides of nitrogen and left a brown oil from which nothing could be isolated; the oil did not give a 2,4-dinitrophenylhydrazone.

(f) 1-Nitro-2-(p-chlorobenzoyl)-3-phenylcyclopropane (X). This substance reacted slowly unless the solutions were moderately concentrated, but the furane was obtained in a yield of 95% by the following procedure: 5 cc. of concentrated sulphuric acid was added to a solution of 5 gm. of the cyclopropane in 75 cc. of acetic acid. Oxides of nitrogen were evolved on warming. After boiling for 10 min. the solution was poured into 400 cc. of water and extracted with ether; on removal of the solvent the furane was left (3.8 gm.). It was recrystallized from methyl alcohol and shown to be 2-phenyl-5-(*p*-chlorophenyl) furane (XVII) by a mixed melting point with a specimen prepared by the method in the literature (19); m.p. 123° C.

Diels and Alder have shown that simple furanes form addition products with maleic anhydride like dienes; this reaction was tried with the above furane but no matter what the conditions, the components were recovered unchanged. Since neither 2,5-diphenyl furane* nor 2,3,5-triphenyl-4-bromofurane formed addition products with maleic anhydride, it would seem that in the furane series the reaction is blocked by two phenyl groups.

(g) Ethyl 1-cyanocyclopropane-1-carboxylate (XII). The ester (5 gm.) was dissolved by stirring in 50 cc. of concentrated sulphuric acid and, after standing overnight, poured into 200 cc. of water. The oil was extracted with ether and thoroughly washed with sodium carbonate solution; on evaporation 2 gm. of the amide (XIX) was deposited, which after crystallizing from methyl alcohol formed thick white rods, m.p. 126° C. Analysis:—Calcd. for $C_7H_{11}O_3N$: N, 8.9%. Found: 8.8%.

The acid-amide (XX) was formed by refluxing for 20 min. 1 gm. of the ester-amide in 5 cc. of 30% aqueous solution of sodium hydroxide and enough alcohol to make a clear solution, pouring into water, acidifying and extracting five times with ether. The solid remaining after removal of the solvent was recrystallized from water, forming rectangular plates, m.p. 190° C. with decomposition. It dissolved instantly in alkaline solutions. Analysis:—Calcd. for $C_5H_7O_3N$; N, 10.8%. Found: N, 10.4%. A trace of another solid was found on ether extraction of the greatly concentrated aqueous solution, and recrystallized from benzene; m.p. 127° C. Analysis:—Found: C, 45.5; H, 5.1; N, 5.5%.†

The acid-amide was hydrolyzed to the known cyclopropane-1,1-dicarboxylic acid (XXI) by refluxing for 20 min. a solution of 2 gm. in 30% aqueous potash. It was isolated by ether extraction after acidification and the usual treatment. It melted at 136° C. and showed no depression when mixed with the acid as obtained by the established method (8).

As a reference compound the di-(*p*-bromophenacyl) ester was prepared. A solution of 0.4 gm. of the acid in 5 cc. of water was neutralized with sodium carbonate and then just barely acidified to litmus with hydrochloric acid; 10 cc. of alcohol was added and water to keep the salt from separating—then 0.8 gm. of *p*-bromophenacyl bromide was introduced and the mixture refluxed for an hour. The ester separated on cooling, and after recrystallization from alcohol formed long needles, m.p. 146° C. Analysis:—Calcd. for $C_{21}H_{16}O_6Br_2$: Br, 30.5%. Found: Br, 29.9%.

(h) 1,3-Diphenyl-2-benzoyl-1-cyanocyclopropane (XIII). Three stereoisomeric forms of this were available from a previous investigation; they all gave the same amide (XXIII). Five grams of the cyclic nitrile (m.p. 166° C.) was dissolved in 50 cc. of concentrated sulphuric acid by mechanical stirring, and left overnight. After pouring into 450 cc. of water the white precipitate

**The experiments with this substance were performed by Mr. C. S. Maxwell.*

†Owing to the small amounts found its structure was not determined; the analysis corresponds to $C_{10}H_{13}O_7N$, or one molecule of amide-acid plus one molecule of di-acid.

was filtered and recrystallized from acetic acid, in long rods, m.p. 179° C.; 2.5 gm. was obtained. Analysis:*—Calcd. for $C_{23}H_{19}O_2N$; C, 80.9; H, 5.6%. Found: C, 81.0; H, 5.3%.

A small amount (0.2 gm.) of an isomeric amide (m.p. 198° C.) was insoluble in the acetic acid, but was purified by the use of methyl alcohol, and found to be identical with the amide prepared in another investigation, by the action of ammonia on the corresponding cyclic ester.†

Isomerization. A mixture of 0.2 gm. of the amide (m.p. 179° C.), one drop of sulphuric acid and 20 cc. of acetic anhydride was kept at 100° C. for two hours, decomposed by iced carbonate and worked up in the usual way. The product was shown to be the isomeric form (m.p. 198° C.) by a comparison of solubilities, melting point and mixed melting point.

The reverse change was brought about by saturating a methyl alcoholic solution of 1 gm. of the amide (m.p. 198° C.) with hydrogen chloride and after several days removing the solvent and crystallizing the residue from benzene; by a comparison of properties and mixed melting point it was found to be the isomer melting at 179° C.

Dehydration. The amide (179° C.) was recovered unchanged after refluxing with thionyl or acetyl chloride. A mixture of 0.5 gm. each of the amide and phosphorus pentachloride in 25 cc. of dry xylene was refluxed for 40 min. The phosphorus compounds were washed out with water and the nitrile (m.p. 166°) crystallized on partial removal of the solvent; it melted at 164–165° and a mixed melting point was 165–166° C. Neither amide was esterified under any conditions.

(i) Diphenylcyclopropyl carbinol (XIV). This substance dissolved in sulphuric acid with the production of an orange-red color, slowly changing to green. It could not be recovered, even on immediate addition of the solution to ice. The oil produced was unsaturated, decolorizing bromine and permanganate, but gave no ester in the Schotten-Baumann reaction. The amount available was too small to make further study practical.

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**For this analysis the writers are indebted to Mr. H. B. Rosener.*
†The results of this work will be published later.

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DIHYDRO-*p*-TOLUALDEHYDE[1]

By C. F. H. Allen[2], W. L. Ball[3] and D. M. Young[4]

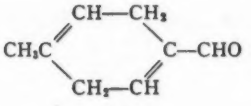
Abstract

In the condensation of acetaldehyde to crotonaldehyde, dihydro-*p*-tolualdehyde is obtained as a by-product. The determination of its structure, its properties and some of its reactions are described.

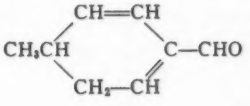
In the manufacture of crotonaldehyde there is always a certain amount of oily residue left in the still. When the residue is submitted to distillation, a yellow oil is obtained. The oil decolorizes bromine and permanganate, and gives an addition product with sodium bisulfite—this would indicate an unsaturated aldehyde or methyl ketone.

Samples of several lots of this oil were placed at the writers' disposal* and the problem of determining the structure of one or more of the substances present was attacked.

When submitted to a slow fractionation *in vacuo*, two main fractions were collected, A(b.p. 68°C. at 10 mm.) and B (b.p. 77°C. at 10 mm.). Both of these decolorize bromine instantly but in a short time evolve hydrogen bromide, reduce permanganate rapidly, form addition products with sodium bisulfite, and reduce Fehling's solution; with semicarbazide, 2,4-dinitrophenylhydrazine, hydrazine, and cyanoacetic acid they both give the same derivatives; therefore they would seem to be unsaturated aldehydes. Upon oxidation with nitric acid, both give *p*-toluic acid; with permanganate the oxidation proceeds to terephthalic acid. In view of these properties the substances are derivatives of dihydrobenzene, having a methyl group in the para position to the aldehyde group. Five structures are thus possible:



(I)



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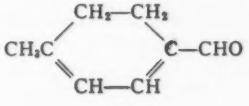

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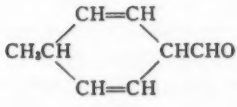

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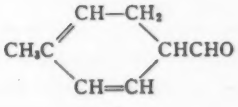

(V)

[1] *Manuscript received July 25, 1933.*
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**Generous specimens of these oils were very kindly furnished by Shawinigan Chemicals Limited, for which the authors express their appreciation.*

Since structures (II, III, and V) contain a conjugated system, a study of the addition products with maleic anhydride or α-napthoquinone might be expected to give a clue as to the nature of the substance, but neither of the fractions reacts, the anhydride or quinone recrystallizing unchanged. The aldehydes do not add to 1,4-diphenylbutadiene. These facts cannot be used to exclude the three structures, for it is only when the Diels-Alder reaction is positive that it is of value in the determination of structure (5). Ozone slowly oxidizes both but the oxidation product is *p*-toluic acid. Autoxidation also gives the same acid.

The distinction between A and B is based entirely on physical properties since in every instance they both give the same derivatives—the identity of the latter was determined by melting points, mixed melting points, solubilities and crystallographic properties.* The reactions forming these derivatives are very rapid and give almost the same yield, though slightly smaller from A. Both A and B are completely soluble in a saturated aqueous solution of sodium bisulfite, but when the aldehyde is regenerated, B alone is found, and its physical properties are slightly different. B is also regenerated from the semicarbazone. This would indicate that A contains some other substance, but so far none has been isolated.

The physical properties are shown in Table I, along with *p*-tolualdehyde and hexadienal for comparison.

TABLE I

Substance	Boiling point, °C.		Density$^{20°}_{4°}$	n^{20}_{D}	Molecular refractivity
	At 10 mm.	At 760 mm.			
A	68	195	1.0035	1.5182	36.854
B	77		1.0150	1.5279	37.006
Regenerated from $NaHSO_3$ compound	77	202	1.0176	1.5408	37.661
p-Tolualdehyde	95	203	1.0297	1.5465	37.546
Hexadienal*	64–6/11	173–4/754	0.9087^{n}_{4}	1.5372^{n}_{D}	

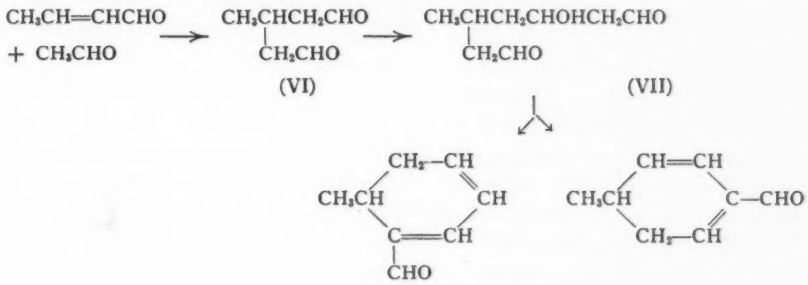
**Octatrienal is a solid, m.p. 55°C., that polymerizes in a few hours (6).*

The aldehyde was condensed with acetone; the product formed had an odor like benzalacetone rather than ionone. Both the pure aldehyde and unsaturated ketone may prove of use to the perfumer.

In a series of three papers (2,3,4) Bernhauer has described certain oils obtained in the preparation of crotonaldehyde under conditions not stated. One was shown to be dihydro-*o*-tolualdehyde, and another, from the meagre evidence given, is doubtless the corresponding para compound here described. In the oils used by the writers there has been no trace of the ortho compound, although a careful examination was made for it. The location of the double bonds in the ortho aldehyde was not determined.

**These were determined by Professor R. P. D. Graham of the Department of Mineralogy, to whom the authors acknowledge their indebtedness.*

A reasonable mechanism that accounts well for the formation of both isomers and that is based on the assumption that acetaldehyde is always present, whether initially or produced by hydrolysis of crotonaldehyde*, is proposed by the present authors as follows: a molecule of acetaldehyde adds to the conjugated system of crotonaldehyde, and the dialdehyde (VI) then adds a second molecule of acetaldehyde, to form (VII). This can condense with itself in two ways, one of which leads to the dihydro-*p*-tolualdehyde and the other to the ortho isomer.



The location of the double bonds is uncertain. One pair is probably conjugated with the side chain carbonyl group since the molecular refraction shows an exaltation (calculated value, if no exaltation = 36.224); because of the ease of removal of two hydrogen atoms, formula (I) may be favored.

Experimental

The aldehyde-containing specimens of oil received were all slowly fractionally distilled in the same apparatus at 10 mm. pressure; a partial condenser containing technical *n*-butyraldehyde was used, to prevent high boiling material from distilling over. It was found that the rate of distillation had a marked effect on the boiling point as registered by the thermometer, superheating being very pronounced. In the apparatus used the containing flask was heated by a hot-water bath, at such a rate that four drops of the distillate every five seconds was collected from the end of the condenser. The apparatus was filled with carbon dioxide. A very small low boiling fraction and the residue were kept separate for future study. Fraction A: b.p. 68° C. at 10 mm.; D_4^{20} 1.0035; n_D^{20} 1.5182. Fraction B: b.p. 77° C. at 10 mm.; D_4^{20} 1.0150; n_D^{20} 1.5279. Both were a very pale yellow but darkened on standing, and had a rather pleasant but very penetrating and slightly soapy odor; this was not present in the aldehyde purified through the bisulfite compound.

Both fractions were shaken with a saturated solution of sodium bisulfite, and the precipitated addition product filtered and washed thoroughly with ether. It was then decomposed by mixing with slightly more than the calculated amount of potassium carbonate, and water, and steam distilling.

**Kuhn has shown that PURE crotonaldehyde is not convertible into hexadienal or octatrienal by catalysts (6).*

The aldehyde was extracted with ether, the extract dried with potassium carbonate and, after removal of the solvent, distilled *in vacuo*. The pure dihydro-*p*-tolualdehyde is a very highly refractive, colorless liquid, possessing a sweet, pleasant odor like *p*-tolualdehyde (or English hawthorn blossoms); b.p. 77° at 10 mm., 202°C. at 760 mm.; D_4^{20} 1.0176; n_D^{20} 1.5408; M_D 37.661 (calcd. M_D for (I) = 36.954). The same constants were obtained with a sample regenerated from the semicarbazone. Analysis:—Calcd. for $C_8H_{10}O$: C, 78.6; H, 8.2%. Found: C, 78.6; H, 8.0%.

Dihydro-*p*-tolualdehyde is easily miscible with the usual organic solvents but does not dissolve appreciably in water, dilute acids, or alkalies. It is charred by concentrated sulphuric acid, and becomes dark brown in the presence of alkalies. It is very easily distilled with steam, the distillate being about one-seventh aldehyde.

It does not give a color with Schiff's reagent, but readily reduces Fehling's solution, especially if a little alcohol is added. It dissolves completely in sodium bisulfite solution; if the solution is saturated, the addition product separates in lustrous leaflets.

This aldehyde very easily undergoes autoxidation, but the process is prevented by addition of a little hydroquinone. It rapidly and instantly decolorizes bromine, but, after a short time, if at all concentrated, hydrogen bromide is given off; under the same conditions *p*-tolualdehyde is unchanged. It consumes far less than the calculated amount of bromine—a similar observation was made by Kuhn with the polyene aldehydes (6)—the amount changing with slight variations in operating; *e.g.*, on the assumption that one mole of bromine per mole of aldehyde is 100%, the following values were obtained (bromide-bromate procedure, or direct titration) 52.95, 34.47, 50.59, 41.43, 33.53, whereas pure *p*-tolualdehyde gave only 0.43.

On heating in an inert atmosphere for several hours it was unchanged; when maleic anhydride or α-naphthoquinone was added and the mixture heated for several hours, there was no reaction, the anhydride and quinone crystallizing on cooling.

The 2,4-dinitrophenylhydrazone was prepared in the usual manner (1). It is very soluble in hot xylene or *p*-cymene, sparingly soluble in hot *n*-butyl alcohol, and insoluble in the other usual solvents; xylene is the best medium for purification. It forms brick-red plates with square ends, m.p. 239°C. Analysis:—Calcd. for $C_{14}H_{14}O_4N_4.H_2O$: N, 17.5%. Found: N, 17.7, 17.9, 17.6%. *p*-Tolualdehyde 2,4-dinitrophenylhydrazone was prepared for comparison; it crystallizes in pointed rods from xylene or cymene, m.p. 206°C.

The semicarbazone, when prepared in the usual manner, formed long transparent needles with square ends. It is moderately soluble in ethyl alcohol but dissolves freely in ethyl acetate. In a capillary tube, it shrinks slightly at about 215°C., melting to a clear liquid at 219°C.; when mixed with the semicarbazone of *p*-tolualdehyde it shrunk at 214° and melted at 217–219°C. Although there is no marked depression of the mixed melting point, the crystals are entirely different in shape, size and other properties.

The *p*-nitrophenylhydrazone was an amorphous substance that could not be crystallized.

The cyano acid; $C_7H_9CH=C(CN)COOH$. A solution of 2 gm. of sodium hydroxide, 30 cc. of water, and 4 gm. of cyanoacetic acid was made slightly alkaline to litmus by adding a little aqueous solution of sodium hydroxide, placed under a stirrer and 5 gm. of the aldehyde introduced. After warming and stirring for three minutes the reaction was completed, and the condensation product was precipitated by addition of concentrated hydrochloric acid. The solid was filtered and recrystallized from dilute alcohol, forming pale yellow needles and rods, m.p. 212-213°C. Analysis:—Calcd. for $C_{11}H_{11}O_2N$: N, 7.4%. Found: N, 7.3%.

The aldazine; $C_7H_9CH=N-N=CHC_7H_9$. A mixture of 5 gm. of hydrazine sulfate, 10 gm. of potassium acetate, and 50 cc. of hot water was cooled slightly, and 50 cc. of alcohol added. The precipitated salt was filtered and 10 gm. of aldehyde was added; the azine separated in a few minutes and was filtered when cold. It was recrystallized from *n*-propyl alcohol, in which it is very soluble hot but practically insoluble cold, forming pale yellow, wedge-shaped prisms, m.p. 157°C. It is insoluble in the cold alcohols, and only sparingly soluble in hot ethyl alcohol, but dissolves readily in ether or hot propyl alcohol. It slowly goes into solution in concentrated sulphuric acid with formation of a bright yellow color.

A cinchoninic acid (from the aldehyde, α-napthylamine, and pyruvic acid) was obtained in such a small yield it was not extensively purified.

Oxidation. (a) *Nitric Acid.* In a 250-cc. three-necked flask fitted with a stirrer and reflux condenser were placed 5 gm. of the aldehyde and the dilute nitric acid made up from 25 cc. of acid (sp. gr. 1.42) and 75 cc. of water, and the whole heated an hour on the steam bath; the *p*-toluic acid separated on cooling. It was filtered, and weighed 3.5 gm. (64%), m.p. 176–177; mixed m.p. 176–177°C.

(b) *Potassium permanganate.* In the same apparatus 40 cc. of acetone, 30 cc. of water and 10 gm. of aldehyde were heated to boiling on the steam bath and 50 gm. of permanganate added in 10-gm. portions as the course of the reaction permitted. After an hour the oxidation was considered completed, though traces of toluic acid were found later on. The oxides of manganese were filtered and extracted with boiling water; on acidification of the filtrate, terephthalic acid was precipitated. It was dissolved in aqueous sodium bicarbonate and reprecipitated by hydrochloric acid; yield, 8 gm. or 66%. For identification a sample was converted into the dimethyl ester by the usual procedure; m.p. 135–137°; mixed m.p. 136–137°C.

(c) *Ozonization.* This was done only qualitatively; after four hours unchanged aldehyde was still present, as shown by removal with sodium bisulfite and formation of the dinitrophenylhydrazone. The alkaline extract of the ethereal solution gave *p*-toluic acid on acidification.

(d) *Autoxidation.* A sample left exposed on a watch glass was nearly solid after three days; the solid was *p*-toluic acid. A similar sample containing hydroquinone was apparently unchanged in the same time.

Condensation with acetone. A mixture of 50 gm. of the aldehyde, 100 cc. of acetone, 500 cc. of water and 10 gm. of barium hydroxide was shaken mechanically for 14 hr., acidified, and steam distilled. The residual oil was taken up in ether and benzene, the extract dried, and after removal of the solvent the unsaturated ketone was distilled in an atmosphere of carbon dioxide; b.p., 177-185°C. at 25 mm. The yield was low (15.3 gm., 23%), there being much high boiling product and tar. The odor resembled that of benzalacetone. The semicarbazone, prepared as usual, crystallized in white rods from ethyl acetate; in a capillary tube it shrunk at 196°, and melted at 206-210°C. with decomposition. Analysis:—Calcd. for $C_{12}H_{17}ON_3$: N, 19.2%. Found: N, 18.5%. The unsaturated ketone gives a bright red color with concentrated sulphuric acid.

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PYROLYSIS OF THE LOWER PARAFFINS

II. THE PRODUCTION OF OLEFINES IN BAFFLED QUARTZ TUBES[1]

By Adrien Cambron[2] and Colin H. Bayley[3]

Abstract

The pyrolysis of the lower paraffins in externally heated quartz tubes has been studied under conditions of streamline and turbulent flow. It has been found possible to produce a high degree of turbulence in the flow of paraffin gases through tubes heated to a high temperature. It has been shown that when the pyrolysis is carried out under conditions of turbulent flow the yields of olefines obtained at a given temperature are greatly increased over those obtained in an open tube. It is further shown that under conditions of turbulent flow higher rates of conversion of the lower paraffins to olefines are possible since the temperatures at which side reactions begin to be noticeable are considerably higher under the above conditions than when the gas flow is streamline.

A considerable amount of work has been done on the effect of such factors as temperature, time of contact and ratio of reaction space to surface on the conversion of the lower paraffins to olefines. The work done on this subject as well as on the use of catalysts has been comprehensively reviewed by Lomax *et al.* (10), their review containing a chronological index of the literature from 1809 to 1915. A later and more elaborate review by Egloff, Schaad and Lowry (5) covers the literature up to 1930. Experiments carried out in these laboratories on the conversion of the lower paraffin hydrocarbons to olefines, by passing the gases over a glowing tungsten spiral or carbon rod, were reported in a previous communication (2).

It is generally accepted that in problems of heat transfer from a solid surface to a gas, one of the controlling factors is the resistance to heat flow of the stationary film of gas which covers the surface. The amount of heat absorbed by the gas in the form of radiation is small, even at the temperatures employed in pyrolysis experiments, so that the greater part of the heat transfer takes place by conduction through the stationary gas film (8,9,14).

The rate of heat transfer between a heated surface and a gas is consequently assumed to depend to a great extent on the thickness of the surface film, which in turn varies to some extent with the viscosity of the gas and with the temperature, but to a greater degree with the character of the gas flow near the surface, for a rapid movement of the gas in this region such as is caused by turbulence, for instance, tends to break down the film.

It is well known that the reactions involved in the conversion of paraffins to olefines are endothermic. Thus the dehydrogenation of the lower paraffins to the corresponding olefines requires about 32,000 calories per gram-mole, whilst the splitting up of the paraffins containing more than two carbon atoms into an olefine and a lower paraffin requires about 16,500 calories per

[1] *Manuscript received August 1, 1933.*
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gram-mole. It follows, therefore, that if a gaseous paraffin (or the vapor of a low-boiling paraffin) be passed through a reaction tube the walls of which are heated to a temperature sufficiently high to cause splitting up of the paraffin into olefines, the amount of reaction taking place after the gas has reached reaction temperature will to some extent be proportional, for a given time of contact, to the rate of heat transfer between the tube wall and the gas. It is known that under certain conditions, for example, at linear velocities greater than a critical value for a tube of a given diameter, the flow of gas in the tube becomes turbulent. It was therefore thought of interest to estimate the critical velocities at which the flow of the lower paraffins changes from streamline to turbulent in a 2.6-cm. tube, such as used in the present experiments.

Using the value of 2,500 for Reynold's number as determined by Stanton and Pannel (12) the critical velocity can be calculated from the following equation:

$$V_c = \frac{2500\,\mu}{d\rho},$$

where V_c is the critical velocity in cm./sec.; μ, the viscosity in C.G.S. units; d, the diameter of the tube in cm.; and ρ, the density of the gas in gm./cc.

Substituting the appropriate values for the lower paraffins, starting with ethane, the values shown in Table I are obtained for a 2.6-cm. tube at room temperatures.

TABLE I

CRITICAL RATES IN 2.6-cm. TUBE AT ROOM TEMPERATURE

Gas	μ	ρ	Linear velocity, cm./sec.	Critical rate in l/hr. in 2.6-cm. tube
Ethane	0.0000929	0.00134	66.5	1270
Propane	.0000806	.00200	39.0	745
Butane	.0000739	.00260	27.0	515

It will be observed that, in the above equation, owing to the concurrent increase in density and decrease in viscosity as the length of the paraffin chain increases, there is a rapid decrease in critical velocity with increase of molecular weight so that if pentane vapor, at 40°C. for instance, were passed through a 2.6-cm. tube at 400 litres per hour the gas flow would be expected to be turbulent.

The rate of thermal decomposition of the lower paraffins becomes rapid at temperatures of 800–1000°C. and it is consequently in this temperature range that the estimation of the critical velocity was believed to be of interest. Knowing the critical velocity at room temperature it is possible to calculate approximately the critical velocity at say 900°C., if one disregards such disturbing effects as convection in that part of the tube where the temperature of the gas is different from the temperature of the tube wall, and assuming that Reynold's number does not vary appreciably with temperature.

It will be observed that, according to the equation:

$$V_c = \frac{2500\,\mu}{d\rho},$$

the expansion of the gas due to increase in temperature will cause an increase in the linear velocity, but also a corresponding decrease in the density, so that, assuming the viscosity to be constant, the critical mass velocity would remain constant. The viscosity coefficient, μ, however, increases rapidly with the temperature, causing a corresponding increase in the critical velocity, so that we have the relation:

$$\frac{(V_c)_T}{(V_c)_o} = \frac{\mu_T}{\mu_o},$$

where $(V_c)_T$, is the critical velocity at temperature T; μ_T, the coefficient of viscosity at temperature T; $(V_c)_o$, the critical velocity at 20°C.; and μ_o, the coefficient of viscosity at 20°C.

Although Sutherland's formula for the variation of viscosity with temperature is not accurate at higher temperatures, its use in this case probably gives a sufficiently close approximation of the value of the critical velocity, and it should give a fairly good idea of the variation of the critical velocity with the molecular weight of the paraffin.

According to Sutherland's formula:

$$\frac{\mu_T}{\mu_o} = \left(\frac{T}{273}\right)^{\frac{3}{2}} \frac{C+273}{C+T}$$

where T is the temperature of the gas, and C, Sutherland's constant.

Table II, shows the values of C taken from Landolt, the value of the viscosity coefficient for each gas at 900°C. as calculated by the above formula, the value of V_c reduced to 20°C. and the critical rate of each gas in litres per hour in a 2.6-cm. tube.

TABLE II

CRITICAL RATES IN 2.6-cm. TUBE AT 900°C.

Gas	C	μ, at 900°C.	V_c, cm./sec.	Rate in litres/hr. in a 2.6-cm. tube
Ethane	287.3	0.000325	232	4440
Propane	241.3	0.000290	140	2680
Butane	377.4	0.000273	100	1900

The increase in critical velocity was considerably higher than was expected and the wide difference between the critical rates and the rates ordinarily used in pyrolysis experiments indicates that the gas flow in unobstructed tubes at temperatures around 900°C. is undoubtedly streamline throughout the greater part of the tube.

Effect of Baffles on the Gas Flow

Preliminary experiments having shown that a series of circular disks placed centrally in the tube were highly efficient in producing turbulence, a series of experiments was carried out to determine the relation between the diameter and the spacing of the disks or baffles and the degree of turbulence produced.

The degree of turbulence was taken as proportional to the loss of kinetic energy of the gas flowing through the baffled tube, this loss being determined by measuring the pressure drop over the length of the tube by means of static pressure tubes connected to manometers.

The following experiments were carried out at room temperature partly for convenience and partly by necessity, since, at the higher temperatures accurate measurements of pressure drop could not have been made.

The first series of experiments (Table III) was carried out with mica baffles 2.3 cm. in diameter in a 2.6-cm. tube of glazed translucent quartz, the baffles being supported on a 0.9-cm. diameter quartz rod which was placed at the axis of the 2.6-cm. tube, the baffled length being 42 cm. The second series of experiments (Table IV) was carried out in the same manner, except that the diameter of the baffles was 2.1 cm. instead of 2.3 cm. In these two tables the first vertical column gives the gas rate in litres per hour, propane being the gas used, and the first horizontal column gives the spacing between the baffles, in centimetres. The other figures give the pressure drop in centimetres of water between the two ends of the tube corresponding to a given rate of 1400 litres per hour; the pressure drop was too small to be measurable on the manometers used.

TABLE III

RELATION BETWEEN PRESSURE DROP, GAS RATE AND BAFFLE SPACING WITH 2.3-cm. BAFFLES

Rate, l/hr.	Baffle spacing, cm.									
	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.8
	Pressure drop, cm. of water									
428	0.33	0.31	0.35	0.35	0.35	0.34	0.34	0.31	0.28	0.23
507	.44	.42	.47	.44	.46	.45	.42	.41	.37	.32
625	.67	.65	.70	.63	.72	.68	.66	.68	.63	.52
730	.89	.85	.94	.89	.96	.92	.90	.96	.84	.70
798	1.11	1.06	1.17	1.05	1.19	1.13	1.13	1.14	1.04	.91
893	1.30	1.25	1.40	1.24	1.43	1.36	1.35	1.37	1.28	1.06
968	1.51	1.46	1.62	1.42	1.65	1.56	1.57	1.59	1.48	1.25
1070	1.82	1.76	1.98	1.75	1.96	1.90	1.94	1.95	1.83	1.53
1170	2.20	2.16	2.41	2.16	2.34	2.30	2.33	2.37	2.24	1.92
1325	2.71	2.75	2.98	2.80	2.98	2.84	2.88	2.94	2.84	2.49
1445	3.08	3.04	3.45	3.33	3.49	3.32	3.33	3.40	3.27	2.90

NOTE:—*2.6-cm. tube.*

TABLE IV

RELATION BETWEEN PRESSURE DROP, GAS RATE AND BAFFLE SPACING WITH 2 1-cm. BAFFLES

Rate, l/hr.	Baffle spacing, cm.			
	0.8	1.2	1.6	2.0
	Pressure drop, cm. of water			
428	0.06	0.08	0.08	0.06
507	.08	.12	.12	.10
625	.11	.16	.18	.17
730	.16	.24	.27	.23
798	.20	.28	.32	.29
893	.28	.36	.39	.38
968	.30	.42	.46	.43
1070	.36	.51	.53	.54
1170	.46	.63	.68	.65
1325	.56	.79	.87	.84
1445	.68	.93	1.02	1.00

NOTE:—*2.6-cm. tube.*

Some of the values obtained in the above experiments have been plotted (Fig. 1). In these curves the log of the pressure drop in centimetres (Log ΔP) has been plotted against the log of the gas rate.

The relation between pressure drop and gas rate and also the fact that the pressure drop is, within limits, independent of the number of baffles, show quite definitely that the baffles produce turbulence in the gas flow when propane is passed through the tube at rates above 400 litres per hour. With regard to the relation between pressure drop (ΔP) and rate of flow (V), when the flow is streamline the pressure drop varies directly with the gas velocity; for a given gas and a given size and length of tube

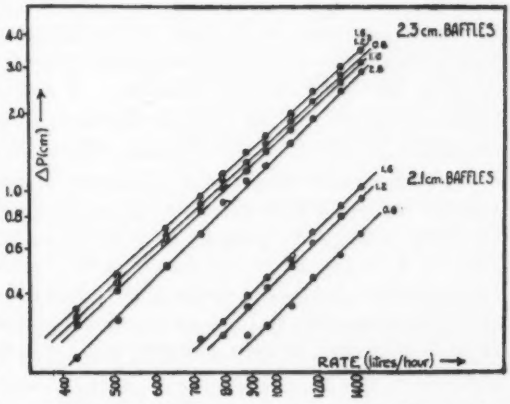

Fig. 1. *Relation between log ΔP and log of gas rate for different baffle spacings and diameters.*

$$\Delta P = KV.$$

When the flow is turbulent, however, the pressure drop varies with the square of the gas velocity

$$\Delta P = KV^2$$

$$\text{or } \log \Delta P = K + 2 \log V,$$

and this is actually the relation that has been found to exist between pressure drop and rate in a baffled tube. It will be observed (Fig. 1) that the plot of log ΔP against log V gives straight lines and that the slope of the curves is very close to 2 (log ΔP is plotted on half the scale of log V) except when the baffle spacing is increased beyond 2.4 cm. The fact that the slope of the curve varies slightly from the theoretical value may be due to defects in the static pressure tubes used to determine the pressure at each end of the baffled tubes. The curves for the 1.4, 1.8, 2.0, 2.2 and 2.4-cm. baffle spacing for the 2.3-cm. baffles have not been plotted because these lie very close to the curves for 1.2-cm. spacing.

The fact that all the curves are parallel show that although the degree of turbulence varies with the spacing and the diameter of the baffles, the flow remains turbulent within the limits used. According to a recent paper by Colburn and King (3) the heat transfer from a heated tube to a gas passing through the tube under conditions of turbulent flow varies with somewhat less than the 4th power of the pressure drop, and in view of this relation between the heat transfer rate and the pressure drop it would be expected that, since the pressure drop does not vary appreciably when the baffle spacing is increased from 1.2 to 2.8-cm., the heat transfer rate and consequently the amount of decomposition which takes place when a paraffin is passed through a heated tube should be more or less constant within these limits.

This has actually been found to be the case as the results of experiments which have been carried out to test this point. These experiments show that varying the baffle spacing between 1.2 and 2.8 cm. had no appreciable effect on the rate of pyrolysis of propane, or on the course of the reaction at a given temperature and at a gas rate of 400 litres per hour.

Furthermore, in view of the relation between pressure drop and heat transfer rate, it will be observed that with the 1.6-cm. spacing, for example (2.3-cm. baffles), the pressure drop increases from 0.35 cm. at 428 litres per hour to 1.19 cm. at 798 litres per hour. According to Colburn and King heat transfer coefficients under these conditions would be expected to vary approximately with the 0.4 power of the pressure drop. Consequently the relation between the heat transfer rates at 798(H_2) and 428(H_1) litres per hour would be:—

$$\frac{H_2}{H_1} = \frac{1.19^{0.4}}{0.35^{0.4}} = 1.6$$

According to these figures, increasing the gas rate in the baffled tube should result in a very considerable increase in the heat transfer rate and consequently, in the degree of pyrolysis of the paraffins; the capacity and current efficiency of a given reaction tube should increase with the gas rate, provided, of course, other factors such as temperature of tube wall and contact time were kept constant.

Thermal Dehydrogenation of Paraffins under Conditions of Streamline and Turbulent Flow

Apparatus

The apparatus used in the present experiments is shown in Fig. 2. The gas pressure was reduced to about 20 lb. by means of a reducing valve and the gas flow regulated through a low pressure valve (*B*) whence the gas passed to the capillary flowmeter (*C*), the wetmeter (*D*), the drying tower (*E*) containing fused calcium chloride and to the furnace *F*. The quartz rod carrying the mica baffles (*G*) was supported usually at three points by triangles of heavy mica sheet mounted on the rod and fitting the tube snugly. The

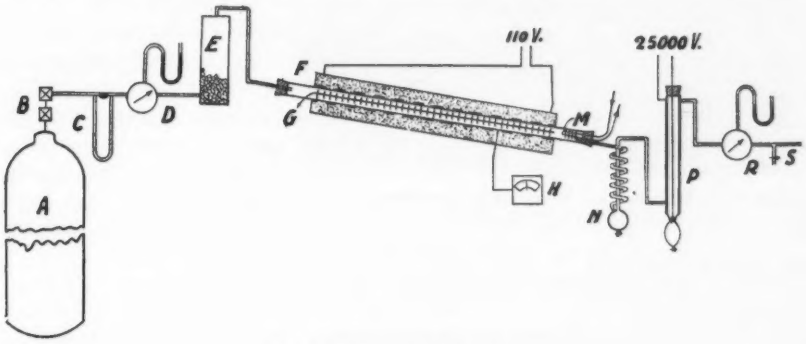

Fig. 2. *Diagram of apparatus.*

gas leaving the furnace was rapidly cooled by means of a loop of $\frac{3}{16}$-in. copper tubing to which a number of copper baffles (*M*) were soldered, and through which cold water was passed. The gas then passed through a spiral glass condenser (*N*) immersed in cold water, an electrostatic precipitator (*P*), and a wet meter (*R*). Samples of the exit gas were taken for analysis through the tube (*S*).

The gas was analyzed over mercury in an Orsat apparatus, the reagents being contained in Francis bubblers. Alkaline mercuric cyanide (13) was used for the determination of acetylene, whilst the butylenes and propylene were determined by absorption in sulphuric acid of 62.4 and 82.5% strength respectively, according to Hurd and Spence's modification (6) of Dobrjanski's method (4). A 4% bromine solution in 10% aqueous potassium bromide was used for the determination of ethylene, the back of the pipette being fitted with a pressure bulb by which the gas could be freed from bro mine vapor by passage into potash before transferring to the burette. Hydrogen was determined by fractional combustion over copper oxide at 300°C. The carbon number of the paraffin residue was obtained by slow combustion in the apparatus described by Bayley (1).

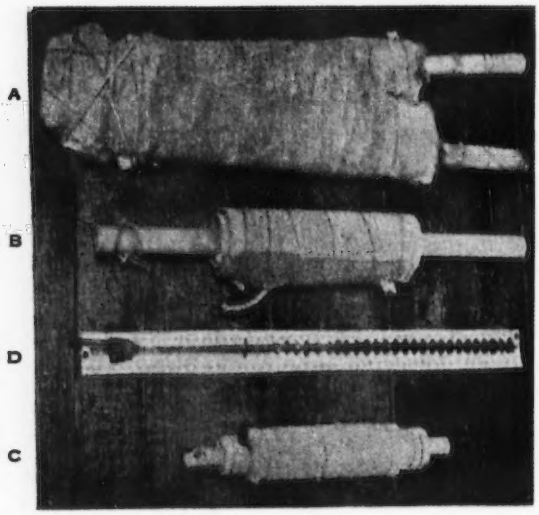

Fig. 3. *Quartz reaction tubes used in these experiments, and a set of baffles for the 80-cm. furnace.*

Fig. 3. shows three of the furnaces and a set of baffles used in the present experiments. (*A*) is the 80-cm. furnace with a tube of 2.5 cm. diameter, (*B*) is the 20-cm. furnace with a tube of 2.7 cm. diameter and (*C*) is the 18.5 by 2.0 cm. tube. (*D*) shows the baffles as used in each section of the 80 by 2.5 cm. furnace.

Gases Used

The ethane, propane and *n*-butane were supplied in cylinders by the Carbide and Carbon Chemicals Corporation. The isobutane used was the commercial grade supplied by the Viking Company of Charleston, West Virginia. The values of n in $C_nH_{2n}+2$ for each paraffin, determined by slow combustion analysis, are given in Table V.

TABLE V

VALUES OF n FOR SAMPLES OF PARAFFINS USED

Gas	Ethane	Propane	*n*-Butane	Isobutane
n	1.93	2.95	3.98	4.07

(*a*) EFFECT OF BAFFLES ON WALL TEMPERATURES

The increase in the rate of heat transfer from tube wall to gas is well illustrated in the following experiments with propane. On passing the gas at the rate of 400 litres per hour through a furnace consisting of a 40 cm. by 2.5-cm. diameter quartz tube the results shown in Table VI were obtained with and without the use of baffles respectively.

TABLE VI

COMPARISON OF PYROLYSIS OF PROPANE IN EMPTY AND IN BAFFLED TUBES AT THE SAME CURRENT INPUT

—	Empty tube	Baffled tube	—	Empty tube	Baffled tube
Gas rate, l/hr.	400	400	Analysis of gaseous product, % by volume		
Current, watts	1113	1113			
Wall temp., °C.	996	918	C_2H_2	1.5	0.3
Expansion, %	55.7	58.9	C_2H_4	20.7	20.7
Gm. olefines per hr.	240.0	301.0	C_3H_6	6.6	11.7
By-products	Liquids and tar	None	H_2	17.1	13.8

The wall temperatures recorded in these experiments were the temperatures indicated by thermocouples placed against the outside surface of the reaction tube, and near the outlet end of the heated section where the wall temperature was highest.

The effect of the turbulence produced by the baffles on the rate of heat transfer between the tube wall and the gas is clearly shown by the difference in the tube wall temperatures in the empty and the baffled tube, the difference being obviously due to the fact that heat is being removed from the wall at a faster rate when the gas flow is turbulent.

It will also be observed that the amount of reaction is about the same in both experiments, although the wall temperature was 78°C. lower in the baffled tube. This shows that under conditions of substantially streamline flow, as the writers have shown to be the case in the empty tube, the recorded wall temperature is that corresponding to the temperature of the stationary gas film in contact with the wall, but is considerably higher than the average gas temperature throughout the reaction chamber.

It will further be observed that the concentration of propylene in the product obtained in the empty tube is only about one-half of the concentration of propylene in the product from the baffled tube. The high percentage of hydrogen and the formation of liquids in the empty tube are due to the polymerization of a portion of the olefines formed.

The same effect is still more strikingly shown in experiments in which a larger furnace and higher gas rate were used.

The following two experiments were carried out in a furnace 80 cm. long and 2.5 cm. in diameter. It consisted of two 40-cm. sections electrically heated by means of nichrome windings, the heating of each section being controlled independently. Baffles (2.2 cm.) were used in the first or preheating section in both experiments and the temperature of the outlet end of this section was maintained at the same point in both cases. Consequently in each experiment the gas entered the reacting section at the same temperature.

In the first experiment no baffles were used in the 40-cm. reactor, whilst in the second experiment 2.2-cm. baffles were used in this section. The results are shown in Table VII.

TABLE VII

TEMPERATURE REQUIRED TO PRODUCE EQUAL EXPANSIONS IN EMPTY AND IN BAFFLED TUBES

—	Empty tube	Baffled tube	—	Empty tube	Baffled tube
Gas rate, l/hr.	801	801	Analysis of gaseous product, % by volume		
Wall temp., preheater, °C.	949	949			
Wall temp., reactor, °C.	1041	946	C_2H_2	2.0	1.1
Expansion, %	84	88	C_2H_4	25.7	26.1
Gm. olefines per hr.	697	821	C_3H_6	8.1	11.7
By-products	Liquids and tar in considerable quantity	None	H_2	19.0	17.5

It will be observed that the difference in wall temperature amounts to 95°C. Since in both experiments the gas entered the reactor at the same temperature, it is believed that these results show conclusively that the temperature distribution in the reactor in the absence of baffles is not uniform and that actually only a portion of the gas is subjected to the high temperature near the wall of the tube; otherwise the amount of reaction in the unbaffled tube would be greater, whilst actually the amount of reaction in the latter tube was less than in the baffled tube at the lower temperature.

(b) Effect of Baffles on the Course of the Reaction

The following two experiments illustrate particularly the effect of turbulence in the gas flow on the course of the reaction when propane is pyrolyzed:—

On passing the gas, at 400 litres per hour through an unbaffled reaction tube and through a baffled tube, both tubes being 40 cm. in length and 2.5 cm. in diameter, it was found that on gradually raising the temperature, a point was reached at which the appearance of a mist in the exit gas indicated the formation of liquid by-products. The expansion observed at this point is referred to as the critical expansion. The results obtained are shown in Table VIII.

TABLE VIII

Critical expansions in empty and in baffled tubes

—	Empty tube	Baffled tube	—	Empty tube	Baffled tube
Temp., °C.	920	981	Analysis of gaseous product, % by volume		
Gas rate, l/hr.	399.1	395.0			
Critical expansion, %	35.1	91.2	C_2H_2	0.6	1.0
Gm. olefines per hr.	180.5	413.5	C_2H_4	16.4	27.7
			C_3H_6	6.9	10.4
			H_2	12.2	17.2

In the empty tube, the polymerization of olefines to liquids began when the wall temperature reached 920°C. at which point the critical expansion was only 35.1%, which corresponds to an olefine content of 23.3%, as shown by the analysis of the products.

In the baffled tube however, at the same gas rate, it was possible to raise the tube wall temperature to 981°C. before there was any evidence of side reactions, the corresponding expansion being 91.2% and the concentration of olefines in the exit gas being 38.1% by volume. Under the above conditions the percentage conversion based on theory of entering propane to olefines, as calculated from the above figures, was 31.5% when an empty tube was used and 72.9% in the case of the baffled tube.

(c) Effect of Baffle Spacing and Baffle Diameter on the Reaction

As we have seen, the pressure drop through a baffled tube is actually due to turbulence and not to the impact of the gas stream on the baffles since, within limits, the pressure drop is independent of the number of baffles used. It was consequently thought of interest to determine the effect of baffle spacing on the conversion of propane to olefines in order to find out whether the same effect would be observed as regards the course of the reaction.

The results shown in Table IX were obtained with a 40-cm. tube of 2.5 cm. diameter, the baffle diameter being 2.25 cm.

TABLE IX

Relation between baffle spacing and critical expansion

Expt. No.	Baffle spacing, cm.	Rate, l/hr.	Temp., °C.	Critical expansion, %	Analysis of gaseous products, % by volume				*n* for paraffin residue	Olefines produced, gm./hr.
					C_2H_2	C_2H_4	C_3H_6	H_2		
1	1.2	395	967	92.7	1.4	27.7	9.5	18.2	1.24	399
2	1.6	396	971	89.7	1.5	27.7	10.1	17.5	1.56	402
3	2.8	398.1	970	87.0	1.6	26.9	10.5	17.5	1.61	397
4	4.0	397.3	990	83.5	1.3	27.3	9.9	17.5	—	384
5	6.0	397.3	987	82.0	1.3	27.0	9.1	17.8	—	354
No baffles		399.1	920	35.1	0.6	16.4	6.9	12.2	—	180

It will be seen that the effect of baffle spacing on the amount of olefines produced per hour begins to be appreciable when the baffle spacing is increased from 1.2 to 4.0 cm., but even at a baffle spacing of 6.0 cm., when the number of baffles is only one-fifth of the number when a 1.2 cm. spacing is used, there is no very marked drop in the amount of olefines produced. In the absence of baffles, however, there is a 50% drop in the amount of olefines produced.

In the above experiments, the temperature was raised until the appearance of a mist in the off-gas indicated the formation of by-products resulting from the polymerization of a portion of the olefines.

The effect of turbulence on the course of the reaction is further illustrated by the results obtained in experiments with ethane, propane and *n*-butane. The following experiments were carried out in a furnace consisting of a glazed quartz tube 2.0 cm. in diameter and having a heated length of 18.5 cm. The wall thickness of the tube was 3 mm. Two series of experiments were carried out with and without baffles respectively, to determine the effect of turbulence on the reaction. In the experiments with baffles, mica disks of 1.7 cm. diameter were used and were mounted on a 0.3 cm. diameter quartz rod, the spacing of the baffles being 1.8 cm. Temperature measurements were made by means of a thermocouple situated 4 cm. from the exit end of the heated section. The results are shown in Table X. Using the empty tube, it was found that the formation of mist began around 900°C. and above this temperature liquids were produced in increasingly large amounts.

TABLE X

PYROLYSIS OF ETHANE IN EMPTY AND IN BAFFLED TUBES

Expt. No.	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
				C_2H_2	C_2H_4	Higher* olefines	H_2	
Empty tube								
6	945	206.3	35.8	0.8	27.6	0.4	29.2	99.4
7	995	208.8	52.0	1.4	26.9	0.9	33.9	113.8
8	1045	208.0	60.8	3.0	24.0	0.9	38.9	108.0
Baffled tube								
9	950	203.8	52.5	0.4	32.6	2.3	35.2	143.7
10	960	208.8	58.1	1.1	33.8	0.2	37.6	141.2
11	980	207.1	67.6	2.1	32.7	1.1	41.2	151.3

**Calculated as butylenes.*

TABLE XI

PYROLYSIS OF PROPANE IN EMPTY AND IN BAFFLED TUBES

Expt. No.	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
				C_2H_2	C_2H_4	C_3H_6	H_2	
Empty tube								
12	902	205.0	35.5	0.6	15.4	6.9	10.1	89.5
13	950	209.7	48.7	0.8	17.9	6.6	12.8	106.9
14	1000	209.7	60.8	1.8	19.0	6.3	16.6	119.9
15	1050	207.2	78.3	2.6	19.2	4.8	21.6	122.1
Baffled tube								
16	860	210.5	54.4	0.5	19.2	12.1	14.2	151.7
17	900	205.4	73.5	0.9	23.1	11.9	16.1	182.4
18	950	206.3	99.6	2.6	27.8	8.8	18.9	211.3

NOTE:—*Length of tube, 18.5 cm.; diameter of tube, 2.0 cm.*

In Experiment 8, in addition to a large amount of mist and tar, there was a considerable deposition of carbon in the reaction tube. The percentage of ethylene in the off-gas decreased with increasing temperature whilst that of hydrogen increased, indicating loss of ethylene by side reactions.

In Experiment 9 there was no evidence of side reactions and even at 960°C. (Expt. 10) there was only a slight amount of mist in the exit gas. Hence the critical expansion can be taken as 58.1%.

The effect of the baffles is indicated by a comparison of the olefine yields in grams per hour. In the unbaffled tube the maximum production was 113.8 gm. per hr. in Experiment 7, whilst the use of baffles resulted in a yield of 151.3 gm. per hr. (Expt. 11) at a somewhat lower tube wall temperature.

Results very similar to those shown above were obtained when the pyrolysis of propane was carried out under conditions of streamline and turbulent flow. The furnace was used in these experiments as in the case of ethane. The data obtained are recorded in Table XI.

Two experiments have been carried out in a furnace 20 cm. long and 2.7 cm. in diameter. The increase in the yield of olefines due to turbulence seems to be somewhat more marked at the temperature and gas rate used in these experiments, the amount of olefines produced per hour being almost doubled when the reaction was carried out in the baffled tube (Expt. 19) as compared to the empty tube (Expt. 20). The results are given in Table XII.

TABLE XII

PYROLYSIS OF PROPANE IN EMPTY AND IN BAFFLED TUBES AT HIGH TEMPERATURES

Expt. No.	Type of tube	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
					C_2H_2	C_2H_4	C_3H_6	H_2	
19	Empty	1032	412	30.5	1.1	16.1	5.2	12.0	161
20	Baffled	1035	404	58.3	0.6	19.1	12.6	14.3	304

NOTE:—*Length of tube, 20 cm.; diameter of tube, 2.7 cm.*

With *n*-butane, which on thermal decomposition gives ethylene and propylene, the absence of side reactions under conditions of turbulent flow is very well illustrated by comparing the percentages of propylene in the exit gas when using the baffled tube with the concentration of this olefine when using the empty tube.

The experiments were carried out with the 18.5 by 2.0 cm. furnace as in the case of ethane and propane and the data obtained are shown in Table XIII. It will be seen that in the absence of baffles the percentage of propylene in the off-gas never exceeded 10·9% (Expt. 22) and in this experiment the formation of a mist indicated a certain amount of side reactions. With the baffled tube there was no mist formation until an expansion of 67.6% had been reached (Expt. 26) and in this experiment the percentage of propylene in the exit gas was 17.0. It will be observed that under these conditions the amount of olefines produced at a given tube wall temperature was very nearly doubled when baffles were used.

TABLE XIII

PYROLYSIS OF *n*-BUTANE IN EMPTY AND IN BAFFLED TUBES

Expt. No.	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.					Olefines produced, gm./hr.
				C_2H_2	C_2H_4	C_3H_6	C_4H_8	H_2	
Empty tube									
21	852	203.8	24.2	0.4	8.9	10.2	1.4	6.2	85.4
22	910	204.6	45.2	0.6	12.4	10.9	1.7	8.1	94.7
23	950	202.1	63.0	0.9	15.8	10.5	2.7	10.7	152.1
23A	990	204.6	78.4	1.6	19.1	10.0	2.2	13.0	175.7
Baffled tube									
24	840	205.4	43.1	0.4	11.8	13.9	2.9	8.1	141.5
25	868	202.1	56.3	0.5	13.7	15.1	2.6	9.8	164.2
26	895	203.8	67.6	0.8	14.9	17.0	1.8	11.2	189.2
27	922	203.8	83.3	1.3	18.3	15.0	2.1	12.6	210.4

Experiments in Baffled Tubes

(1) *Ethane*

In addition to the experiments recorded above, the following experiments were carried out to determine the effect of varying the time of contact and temperature on the yield of olefines in a baffled tube.

The first experiment was carried out in a 20-cm. furnace with a tube of 2.5 cm. diameter. The next five experiments were carried out in a 40-cm. furnace with tubes of 2.7 cm. and 2.5 cm. diameter, and the last two experiments in an 80-cm. furnace with a tube of 2.5 cm. diameter. The data are shown in Table XIV.

TABLE XIV

EFFECT OF TEMPERATURE AND TIME OF CONTACT ON THE PYROLYSIS OF ETHANE IN BAFFLED TUBES

Expt. No.	Length of tube, cm.	Diam. of tube, cm.	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.			Olefines produced, gm./hr.
						C_2H_2	C_2H_4	H_2	
28	20		1091	400.6	66.5	1.0	33.8	35.6	282
29	40	2.7	951	408.0	57.8	0.5	34.7	35.7	280
30	40	2.7	973	406.0	69.8	0.9	35.0	39.6	302
31	40	2.5	933	385.4	60.5	0.3	32.4	35.2	279
32	40	2.5	965	409.2	70.3	0.7	33.4	37.4	308
33	40	2.5	995	397.3	79.5	1.6	32.9	38.8	300
34	80	2.5	916	807.0	46.8	0.3	31.2	31.1	483
35	80	2.5	940	842.0	59.0	0.4	33.1	34.2	577

The absence of side reactions in the above experiments is very well shown by the close agreement between the concentrations of ethylene and hydrogen in the gas produced.

(2) *Propane*

Similar experiments were carried out with propane. As indicated in Table XV, the first experiment was carried out with a 20-cm. furnace, the others with a 40-cm. or 80-cm. furnace. In all experiments the diameter of the tube was 2.5 cm.

TABLE XV

EFFECT OF TEMPERATURE AND TIME OF CONTACT ON THE PYROLYSIS OF PROPANE IN BAFFLED TUBES

Expt. No.	Length of tube, cm.	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
					C_2H_2	C_2H_4	C_3H_6	H_2	
36	20	1087	402.5	76.4	1.4	22.6	13.3	15.4	377
37	40	918	396.5	58.9	0.3	20.7	11.7	13.8	301
38	40	960	396.5	80.7	0.5	24.8	11.0	15.4	370
39	40	981	395.0	91.2	1.0	27.7	10.4	17.2	409
40	40	992	609	63.9	0.8	22.6	11.3	14.8	495
41	40	1020	616	75.0	1.2	25.4	11.2	16.5	572
42	40	992	707	52.0	0.3	19.3	11.2	13.7	488
43	40	1020	705	61.2	0.5	21.5	11.5	15.0	550
44	80	885	417	85.0	1.4	26.8	11.6	17.8	425
45	80	900	510	85.1	1.2	26.9	11.3	14.7	518
46	80	919	607	89.0	1.4	26.2	12.5	17.3	646
47	80	934	708	89.8	1.0	26.2	11.9	17.5	746
48	80	947	801	88.1	1.1	26.1	11.7	17.5	823
49	80	955	700	101.0	1.6	28.6	10.1	17.9	770
50	80	844	807	40.0	0.1	14.0	9.9	11.1	422
51	80	872	801	51.6	0.4	17.6	10.5	13.6	507
52	80	896	807	63.2	0.4	20.0	12.5	14.5	639

The temperature required to convert about 70% of the entering propane to olefines varies with the length of the reaction tube as shown in Table XVI.

TABLE XVI

RELATION BETWEEN LENGTH OF TUBE AND TEMPERATURE

Expt. No.	Length of tube, cm.	Temp., °C.
36	20	1087
38	40	960
44	80	885

The temperatures were recorded by means of a thermocouple placed at a distance of 6 to 10 cm. from the exit end of the heated section.

The thermocouple was placed against the outside surface of the quartz tube and between two windings, the thermocouple being held in place by means of alundum cement, the entire furnace being well insulated with asbestos.

It will be seen that the temperature at which a high rate of conversion of paraffins to olefines takes place has been considerably lowered by the use of baffles in the reaction tube. In Experiment 44, for instance, at a gas rate of 417 litres of propane per hour, over 70% of the entering propane was converted

to olefines at 885°C. This suggested the possibility that heat resistant alloy steel tubes could be used for carrying out this reaction. This phase of the investigation will be the subject of a later communication.

(3) *n-Butane*

A number of experiments were carried out with *n*-butane, some in the 40 by 2.5 cm. tube and the others in the 80 by 2.5 cm. tube. It will be observed that the temperature required for a given conversion of the paraffin to olefines was appreciably lower than in the case of either ethane or propane. The results of the experiments with *n*-butane are given in Table XVII.

TABLE XVII

EFFECT OF TEMPERATURE AND TIME OF CONTACT ON THE PYROLYSIS OF *n*-BUTANE IN BAFFLED TUBES

Expt. No.	Length of tube, cm.	Temp., °C.	Gas rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.					Olefines produced, gm./hr.
					C_2H_2	C_2H_4	C_3H_6	C_4H_8	H_2	
53	40	881	396.5	61.9	0.2	14.5	16.8	5.0	11.4	399
54	40	913	399.0	80.8	0.7	16.5	18.4	4.3	12.7	473
55	40	940	397.5	97.6	1.1	18.7	18.4	3.1	13.6	515
56	80	827	808	41.0	0.2	9.2	12.6	4.4	7.7	545
57	80	858	812	58.0	0.2	11.5	14.7	5.0	9.4	700
58	80	898	808	73.7	0.6	14.0	16.3	5.8	9.7	879
59	80	915	808	88.1	0.6	15.8	17.3	5.3	11.7	995

(3) *Isobutane*

The two series of experiments recorded in Table XVIII were carried out in the 20-cm. and the 40-cm. furnace respectively.

There are indications that the isobutane used in these experiments contained considerable amounts of *n*-butane, possibly up to 40%. Consequently the above figures cannot be regarded as truly representing the results obtainable by the pyrolysis of pure isobutane in the baffled tube. It is expected that with the pure paraffin, the concentration of propylene in the product would be appreciably higher, especially at the lower temperatures.

TABLE XVIII

EFFECT OF TEMPERATURE ON PYROLYSIS OF ISOBUTANE IN BAFFLED TUBES

Expt. No.	Length of furnace, cm.	Diam., cm.	Temp., °C.	Rate, l/hr.	Expansion, %	Analysis of gaseous products, % by vol.					Olefines produced, gm./hr.
						C_2H_2	C_2H_4	C_3H_6	C_4H_8	H_2	
60	40	2.7	1089	401.5	75	.08	15.9	15.7	4.7	13.8	397
61	40	2.7	1100	406.0	81	1.2	17.1	15.2	4.4	14.5	413
62	40	2.5	942	398	124	2.0	21.3	13.7	3.3	16.5	492
63	40	2.5	947	401.5	121	2.5	20.2	14.9	3.8	16.1	516
64	40	2.5	913	400.5	102	2.3	17.2	17.0	4.8	14.8	490

Experiments with Liquid Paraffins

Several experiments have been carried out in baffled reaction tubes on the pyrolysis of the three lower liquid paraffins. In all of these experiments, except in No. 75, a furnace 20 cm. long by 2.7 cm. diameter has been used, the latter experiment being carried out in a 40-cm. furnace, with a tube 2.5 cm. in diameter.

These experiments were characterized by the absence of tar formation and carbon deposition, in spite of the high temperatures used, and the high concentration of olefines in the products obtained.

(5) *Pentane*

The two last experiments of the pentane series (Table XIX) were carried out with pure isopentane, the others with *n*-pentane. It will be observed that there is an appreciable increase in the concentration of the butylenes when the iso-compound is used.

TABLE XIX

Pyrolysis of *n*-pentane and isopentane in baffled tube

Expt. No.	Temp., °C.	Liquid rate, gm./hr.	Gas rate out., l/hr.	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
				C_2H_4	C_3H_6	C_4H_8	H_2	
65	1015	1206	580	20.7	18.5	—	8.1	351
66	1070	1404	615	24.3	17.6	—	8.9	392
67	1075	1158	698	24.0	20.3	1.1	9.5	475
68	1071	1080	667	26.7	20.3	1.5	12.1	475
69	1072	1105	645	20.7	19.9	3.5	11.1	465
70	1075	1080	668	19.4	18.9	4.5	11.3	474

(6) *Hexane*

The hexane used had the following composition:—2-methyl pentane, 40; 3-methyl pentane, 20; *n*-hexane, 30; pentanes and heptanes, 10%.

All of the experiments with hexane (Table XX) were carried out in the 20-cm. furnace with a tube 2.7 cm. in diameter, except in the case of the last experiment in which the furnace used was 40 cm. by 2.5 cm. diameter.

TABLE XX

Pyrolysis of mixed hexanes in baffled tube

Expt. No.	Temp., °C.	Liquid rate, gm./hr.	Gas rate out., l/hr.	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
				C_2H_4	C_3H_6	C_4H_8	H_2	
71	1032	910	555	27.1	23.1	3.3	10.4	480
72	1043	1310	527	26.8	27.9	—	11.0	451
73	1082	864	617	28.6	20.4	—	11.8	448
74	1081	872	618	30.0	21.6	—	11.5	442
75	952	905	694	29.0	19.7	2.1	12.3	544

(7) *Heptane*

The heptane used was of the commercial grade. These experiments were all carried out in the 20-cm. furnace with a tube of 2.7 cm. diameter. The results in Table XXI show that the pyrolysis of the lower liquid paraffins can be controlled so as to yield gaseous products containing between 50 and 55% by volume of olefines. The olefines consisted of approximately equal amounts of ethylene and propylene.

TABLE XXI

PYROLYSIS OF COMMERCIAL HEPTANE FRACTION IN BAFFLED TUBE

Expt. No.	Temp., °C.	Liquid rate, gm./hr.	Gas rate out, l/hr.	Analysis of gaseous products, % by vol.				Olefines produced, gm./hr.
				C_2H_4	C_3H_6	C_4H_8	H_2	
76	1043	1060	487	27.6	24.2	2.9	10.8	426
77	1075	1042	562	29.0	24.5	1.5	11.4	483
78	1093	767	596	31.6	12.5	0.6	16.8	384

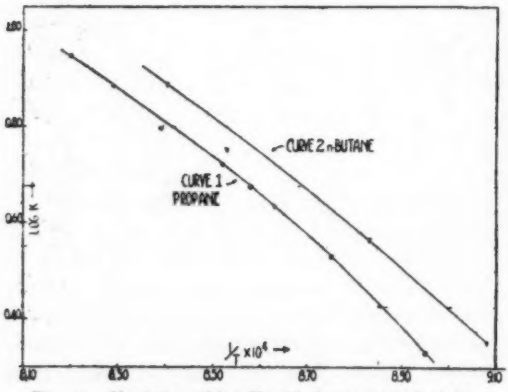

Fig. 4. *Variation of log K with the reciprocal of the absolute temperature.*

The results obtained with the lower liquid paraffins indicate that probably similar results could be obtained by the pyrolysis of the higher boiling members of the series under the same conditions. It is proposed to investigate this phase of the problem in the near future.

Propane Experiments

Increasing the temperature at constant gas rate. The results obtained in the propane experiments 50, 51, 53 and 48 are given in Table XXII. The values of log K and $1/T$ calculated from these experiments have been plotted in Curve 1 (circles). Fig. 4.

TABLE XXII

VALUE OF K FOR PROPANE AT DIFFERENT TEMPERATURES AS CALCULATED FROM EQUATION (1)

Expt. No.	T	$a-x$	t	K	Log K	$1/T \times 10^4$
50	1117	66.1	0.194	2.14	0.3303	8.95
51	1143	54.2	.182	3.38	.5289	8.75
53	1167	45.3	.169	4.71	.6730	8.58
48	1220	28.7	.145	8.85	.9469	8.20

Increasing both the temperature and the gas rate. In the following experiments, the rate was gradually increased from 400 to 800 litres per hour, the temperature being so regulated that the amount of decomposition was about the same in each experiment. The results obtained in this series of experiments are shown in Table XXIII, and the values of log K plotted against the values of $1/T$, in Curve 1, Fig. 4 (squares).

TABLE XXIII

VARIATION OF K WITH TEMPERATURE FOR EQUAL VALUES OF $(a-x)$

Expt. No.	T	$a-x$	t	K	Log K	$1/T \times 10^4$
44	1158	26.8	0.310	4.13	0.6335	8.63
45	1173	28.0	.244	5.26	.7210	8.52
46	1192	25.4	.205	6.26	.7966	8.39
47	1207	27.6	.167	7.68	.8859	8.29
48	1220	28.7	.145	8.85	.9470	8.20
		Mean 27.7				

Temperature coefficient of K for propane. The velocity constant of the decomposition of propane into ethylene and propylene is increased 1.231 times per 10°C. rise in temperature at 845°, and 1.095 times per 10° rise at 940°C.

Butane Experiments

Increasing temperature. The results obtained in a series of butane experiments are given in Table XXIV. The calculated values of log K and $1/T$ are plotted in Curve 2, Fig. 4 (triangles).

TABLE XXIV

VALUE OF K FOR BUTANE AT DIFFERENT TEMPERATURES AS CALCULATED FROM EQUATION (1)

Expt. No.	T	$a-x$	t	K	Log K	$1/T \times 10^4$
56	1101	64.5	0.195	2.25	0.3522	9.08
57	1131	52.6	.175	3.66	.5635	8.83
58	1171	40.2	.161	5.65	.7521	8 53
59	1191	31.4	.150	7.70	.8865	8.40

The temperature coefficient of K for butane is very closely the same as for propane between 845° and 940°C.

Velocity Constants and Temperature Coefficients of the Rate of Conversion of Propane and *n*-Butane to Olefines

It was thought of interest to calculate the velocity constants and the temperature coefficients of the reaction rates from the results obtained in the baffled 80-cm. reaction tube, since a considerably higher amount of decomposition can be obtained under these conditions without appreciable side reactions than with open tubes.

R. N. Pease and E. S. Durgan (11) have shown that the decomposition of propane and *n*-butane is unimolecular and homogeneous and consequently the velocity constant can be calculated by the following formula,

$$K = \frac{2.303}{t} \log \frac{a}{a-x}, \qquad (1)$$

where K is the velocity constant of formation of ethylene and propylene; t, time of contact in seconds; a, the amount of hydrocarbon at the start; and $a-x$, the amount of hydrocarbon remaining after time t.

With regard to the estimation of the time of contact, the fact that the two halves of the reaction tube were heated separately made it possible to bring the gas up to reaction temperature in the first half of the tube, and to maintain a uniform temperature in the second half. The volume of the reaction chamber was consequently taken as half of the total volume of the tube, that is, 202 cc. The volume of the gas passing through the tube was of course corrected for thermal expansion, and for the expansion due to the reaction.

Variation of K and E with Temperature

It will be observed that the change in slope of the curves indicates an abnormal falling-off in the value of K as the temperature is increased. The abnormal decrease in the velocity constant K observed in these experiments may be due to the fact that at the high temperatures used the rate of the reverse reaction, in particular the rehydrogenation of the olefines, begins to be appreciable compared with the forward reaction. Pease and Durgan (11), observed an abnormal decrease in the rate of decomposition of propane and *n*-butane at temperatures as low as 625°C. at a time of contact of 12 sec. This they believe was due to the rehydrogenation of some of the olefines. It should be noted, however, that although *n*-butane gives a product in which the concentration of hydrogen is considerably lower than in the case of propane, yet its rate of decomposition falls off to about the same extent as the rate of decomposition of the latter.

The heat of activation of the decomposition of propane and *n*-butane has been calculated at 850°C. from the slopes of the two curves, which are almost identical at this point. The value found was 45,000 calories. This is considerably lower than the value calculated by Pease and Durgan for the same reaction, their value being 63,000 calories at 625–630°C., but this difference of course was to be expected in view of the very marked decrease in the temperature coefficient with rising temperature, in the range investigated in the present experiments.

Thermal Efficiency of the Baffled Tube

It has already been pointed out that one would expect a definite increase in the rate of heat transfer from tube wall to gas as the gas rate in the baffled tube is increased. Partly in order to test this out and also to determine the relation between the amount of heat required to bring the paraffin up to reaction temperature and that used up in the reaction, a heat balance was calculated for several of the above experiments.

The following heats of reaction were used in the calculation. These figures were calculated from data in Landolt and International Critical Tables, or estimated when heat of combustion data were lacking.

$C_2H_6 \longrightarrow C_2H_4 + H_2$ — 32000 cal. per gram-mole.
$C_3H_8 \longrightarrow C_3H_6 + H_2$ — 32000 cal. per gram-mole.
$C_3H_8 \longrightarrow C_2H_4 + CH_4$ — 16100 cal. per gram-mole.
$n\text{-}C_4H_{10} \longrightarrow C_4H_8 + H_2$ — 32000 cal. per gram-mole.
$n\text{-}C_4H_{10} \longrightarrow C_3H_4 + C_2H_6$ — 17000 cal. per gram-mole.
$n\text{-}C_4H_{10} \longrightarrow C_3H_6 + CH_4$ — 17600 cal. per gram-mole.

Table XXV shows the thermal efficiency of the 80-cm. tube in the decomposition of ethane, propane and *n*-butane. In Table XXV the letters have the following significance:—W = total heat supplied, in kwh.; H = heat absorbed in formation of the amount of olefines found in product of reaction, in kilocalories; $W_1 = H$, in kwh.; W_2 = heat lost through insulation of furnace; $W_3 = W - (W_1 + W_2)$ = heat taken up by the gas when temperature is raised to T; $T.E.$ = thermal efficiency, $= \frac{W_1}{W} \times 100$.

The falling-off in the thermal efficiency of the tube with increasing molecular weight of the hydrocarbon may be explained by the increasing amount of heat required to raise the gas up to reaction temperature, as can be seen by comparing the values of W_1, W_2 and W_3 in Table XXV. In the ethane experiment, for instance, the heat absorbed in the reaction (W_1) is nearly equal to the heat required to heat the gas to reacting temperature (W_3). With propane W_1 is about one-half of W_3, whilst for *n*-butane W_1 is about one-third of W_3.

TABLE XXV

THERMAL EFFICIENCY OF THE 80-cm. TUBE IN THE PYROLYSIS OF ETHANE, PROPANE AND BUTANE

Expt. No.	Gas	Temp., °C.	W, kwh.	Olefines formed, gm.	H, kilocal.	W_1	W_2	W_3	$T.E.$, %
						kwh.			
35	Ethane	940	2.377	C_2H_4, 577	660	0.767	0.735	0.855	32.4
48	Propane	947	2.682	C_2H_4, 450 C_3H_6, 336	515	.598	.755	1.329	22.4
59	*n*-Butane	918	2.946	C_2H_4, 297 C_3H_6, 492 C_4H_8, 201	501	.581	.695	1.670	19.7

Current Consumption in the Production of Olefines in the 80-cm. Furnace

Some values for current consumption in the production of olefines by the pyrolysis of ethane, propane and *n*-butane in an 80-cm. baffled tube are given in Table XXVI.

TABLE XXVI

CURRENT CONSUMPTION IN THE PYROLYSIS OF ETHANE, PROPANE AND *n*-BUTANE IN BAFFLED TUBES

Expt. No.	Hydrocarbon	Gas rate, l/hr.	Temp., °C.	Current, watts	Olefines produced gm./hr.	Kwh./lb. olefines
47	Propane	708	934	2429	746	1.48
48	Propane	801	947	2690	823	1.48
34	Ethane	807	916	2080	483	1.95
35	Ethane	842	938	2377	577	1.86
58	*n*-Butane	808	898	2744	879	1.42
59	*n*-Butane	808	913	2946	995	1.34

The current consumption for the production of olefines in a baffled tube is remarkably low, especially when a comparison is made with the current consumption for the commercial production of acetylene by the carbide process in which 4.5 kwh. are required per pound of acetylene produced. This is interesting in view of the fact that acetylene has been considered as a possible material for the production of ethylene (7, 15).

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